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Faculty of Science

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Silver top-contact deposited onto monolayers incorporating behenic acid and an oligo (phenylene ethynylene) derivative

Final Masters Project

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Certify:

That the work presented is the Final Master Project of Hugo A. Oliva Duarte enrolled in the Masters program of Nanostructured Materials for Nanotechnological Applications and conveys the title "*Silver Top-Contact Deposited onto monolayers incorporating behenic acid and an oligo (phenylene ethynylene) derivative*", which has been carried out in the laboratories of the Institute of Nanoscience of Aragón and the Department of Physical Chemistry of the Science Faculty of the University of Zaragoza, under the direction of both therefore authorizing the presentation of this work for its evaluation by the corresponding examiners.

In witness thereof, this document is issued in Zaragoza, February 1st, 2013

Signed: Pilar Cea Mingueza

Signed: Santiago Martín Solans

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Chapter 1: Introduction and Objectives

Section 1.1: Current Industrial Trends in Micro-and Nanoelectronics

In 1965 the co-founder of Intel, Gordon E. Moore noted that the number of components in integrated circuits (IC) had doubled every year from 1958 till 1965, and predicted that the trend would continue for the next 10 years. In his original statement published in the Electronics Magazine the 19th of April of 1965 Moore stated:

"The complexity for minimum component costs has increased at a rate of roughly a factor of two per year... Certainly over the short term this rate can be expected to continue, if not to increase. Over the longer term, the rate of increase is a bit more uncertain, although there is no reason to believe it will not remain nearly constant for at least 10 years. That means by 1975, the number of components per integrated circuit for minimum cost will be 65,000. I believe that such a large circuit can be built on a single wafer."

In 1975 looking back at his original prediction Moore changed his vision by increasing the time that it takes to double the components and calculations per second of ICs to two years (figure 1). This prediction is known today as Moore's first Law[1, 2] (see Figure 1)**.** . Moore's second law states that as the cost of computer power to the consumer falls, the cost for producers to maintain Moore's law has an opposite trend. Today's current microelectronic innovations such as Intel's 3-D trigate transistor are manufactured at 22 nm[2]. Decreasing the size of transistors enables more power efficiency and increase in processing speed, thus increasing the quality of any electronic device containing a microprocessor.

The current aim of mayor players in the microelectronic industry such as Intel and Globalfoundries is to launch production of a 14 nm transistor based integrated circuit by 2014. With such small scale inorganic circuits it is possible to speculate that silicon based devices will soon reach their physical limit. As of December of 2005 the International Technology Roadmap for Semiconductors (ITRS), officially stated that molecular electronic components will need to be integrated into silicon manufacturing by about 2015 in order for Moore's Law to continue to

hold[3]. The current top-down approach of creating ICs is very costly, and as the density of transistors packed into a given area increases so does the chance of manufacturing defects.[4]

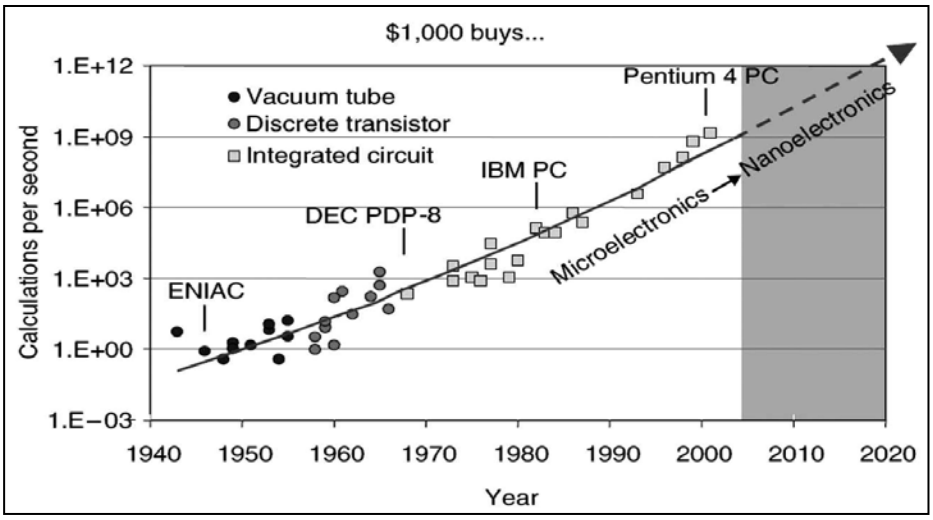


Figure 1: The graph represents the prediction made by Gordon E. Moore; the calculations per second double every couple of years.[4]

Section 1.2: Molecular Electronics as a Future Alternative

One of main challenges faced by the semiconductor industry is to continue downscaling conventional complementary metal-oxide semiconductors (CMOS). The ultimate channel length will be in the range of 10-25 nm, limitation that is due to thermal injection, channel breakdown, doping, and difficulty of interconnection.[4] To overcome this "brick wall" and continue Moor's law it will be necessary to look into an alternative technology such as molecular electronics. This technology is quickly turning out to be the most upholding approach to bypassing conventional CMOS technology.

Since photolithography, which is the standard chip manufacturing technology, does not work at the single molecule range; a notable and current endeavor of molecular electronics is to produce assembly techniques of monomolecular junctions capable of replacing conventional CMOS technology. Some of the molecular junctions reported so far can be positioned into two main categories. In the first category are the individual junctions which are great for studies, but have the disadvantage that their design is not well-suited for the development into arrays of

junctions. The study of such junctions does give a preview of the distinctiveness and behaviors of molecules; it is known that two closely related junctions can have different behaviors due to slight assembly differences. The second category is based on arrays of junctions, nonetheless these kinds of junctions are very difficult to fabricate and many times these are not reproducible by others.[5]

Creating reproducible arrays of molecular junctions will aid to preserve the cost-effective, massively parallel process of the CMOS industry. In order to develop a hybrid system that incorporates molecular nanowires in between metallic electrodes, it is necessary for the molecular components to be compatible with current CMOS fabrication process.[6] Some hybrid CMOS have already been subject to experimentation (*see Section 1.5: Experimental Hybrid CMOS*). Understanding the capabilities of molecular electronics and the limitations of current inorganic based technology will be the base for hybridization of these technologies.

In 2011 the ITRS described the challenges needed to be tackled in order to consider molecular electronics as a viable option for further development of the microelectronic industry. Some of the notable challenges mentioned include the fabrication of low potential barrier electrical contacts, reliable operation, high resistance of molecules in their "on" state, and deposition of top contacts that do not change the molecular properties. Although some molecular devices show promise due to their non-linear intensity vs. voltage curves (*I-V)* and bi-stable behavior, their electrical feat seems to be subject of high potential barriers of the molecule-electrode contact or defect-like processes.[3] In order to guarantee the impact of this field for any future industrial process it is necessary to have a reliable form of fabrication. These fabrication techniques must identify molecule/substrate contacts as well as top contacts with reproducible deposition processes that yield high quality electrical contacts

Section 1.3: Framework of Molecular Junctions

Molecular electronic devices consist of a single molecule or an array of molecules, which are located in between two conducting electrodes. The molecule-metal union is best known as a molecular junction (Figure 2).

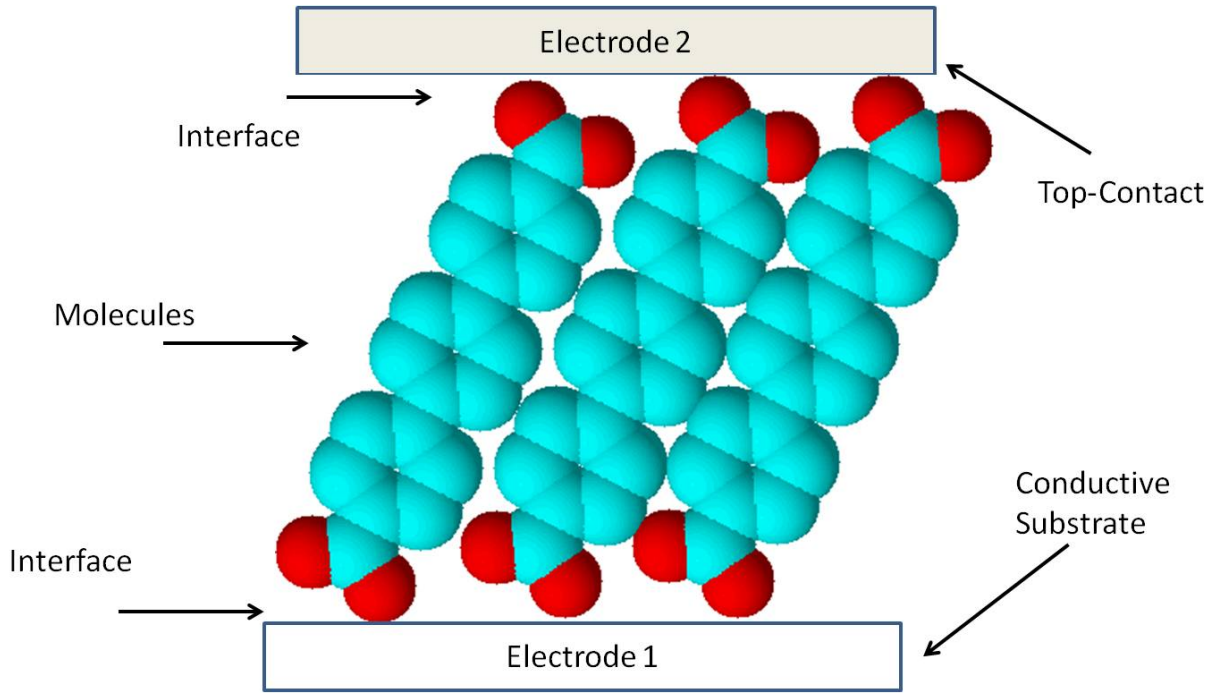


Figure 2: Molecular Junction, with its respective labeled components.[7]

The region in between the interface of molecular junction can be formed by several types of molecules including: aliphatic, aromatic, and organo-metallic complexes. Broadly the materials present in the molecular device can be divided into three parts; 1) the active group which anchors the molecule to the conductive substrate, 2) the conductive skeleton of the molecule, 3) the upper functional group which interacts with the top electrode. Since aromatic compounds and these derivatives have electronic resonance, they are more suitable for electron transport than the mentioned counterparts. In addition, the energy level of aromatic compounds is close to the Fermi energy level of most common inorganic contacts, making these molecules highly interesting for electronic and optical applications.[7]

Within the literature there are several mentioned ways to build a monomolecular layer onto a substrate; however, there are roughly three prominent ones. These techniques are: the self-assembly method (SAMs), Si-C covalent bonding, and the Langmuir Blodgett (LB) technologies. For the purpose of this work the Langmuir Blodgett method will be used.

The molecular junction is made up of molecules, which are either chemisorbed of physisorbed onto the electrodes. The interaction between the molecule and contact is due to the

ability of both parts to form a bonding interaction. Depending on the device assembly technique the interface bonding interaction can vary from strong covalent bonds to weak van der Waals forces. For this reason the electronic performance of the molecular junction is highly influenced by the interface, sometimes even having a greater impact than the molecule used. To interpret current flow through the molecular junction the Launder formula is given[8]:

$$G = \frac{2*e^2}{h} \cdot T_{top} \cdot T_{mol} \cdot T_b \quad (1)$$

In Equation 1 G is the conductance, e is the elementary charge, h is Planck's constant and T_{top}, T_b and T_{mol}, and are the transmission coefficients of the top contact, bottom contact and molecule respectively. As it can be observed if there is a change in value of one of the contacts there is will be a change in current by the same factor.

Currently the scientific community and the ITRS (*Section 1.2: Molecular Electronics as a Future Alternative*) have remarked the need to develop reproducible and reliable molecular devices, mentioning as an interesting topic, the deposition of top contacts that do not change the molecular and electric properties of the junction. The following section continues the description of these molecular electronic devices, but focuses on the main topic of this research project, which is the fabrication of a top-contact onto a monomolecular layer.

Section 1.4: Techniques for Deposition of Top Contacts onto Monomolecular Layers

There are roughly two methods used to create a molecular junction. The first method requires for the molecule to assemble in between a set of electrodes. The second method consists of assembling the monomolecular film onto the substrate, subsequently having the top-contact deposited onto the monolayer. The first method is quite complicated to obtain and reproduce due to the consigned space within which the molecules must interact. The second method although more feasible, still carries with it an important challenge, which is the need to create a top-contact that will not damage or alter the monomolecular layer and will not filter within. The second method is the foundation of this project.

As mentioned in *Section 1.2: Molecular Electronics as a Future Alternative* there are roughly two categories of junctions: the individual junction and an array of junctions both have their respective experimental advantages and disadvantages The main disadvantage of the single

molecular junction is the fact that two closely related junctions can have different behaviors due to slight assembly differences. For this reason and to stay within the objectives of the ITRS and mainstream research, top-contact techniques, i.e., single molecule conductance via break junction, SPM, and c-AFM amongst others will not be discussed further.

There are different top-contact fabrication techniques which have their respective advantages and disadvantages being the common one the penetration of atoms of the metallic layer into the monolayer leading to short-circuits.. The following sub-sections will give a brief overview of the most relevant fabrication techniques. An important factor to reconsider is that the electronic coupling between the molecules and the contacts at both contact/molecule interfaces depends on the techniques used to fabricate the device.

Section 1.4.1: Mercury Drop

This relatively straightforward method of creating a top-contact uses a drop of mercury deposited directly onto a monomolecular layer. A main advantage of this method is its simplicity. Moreover, the drop does not penetrate the monomolecular layer due to the high surface tension of the mercury drop. It is possible via an optical microscope to determine the area of contact of the mercury drop, and given this information the amount of molecules in direct contact with the electrode can also be calculated. With this method it is only possible to determine the conductance on the array of molecules. A disadvantage encountered by this method is the lack of steady endurance of the electrode, due to its liquid state.[9] Finally literature results have mentioned the possibility of defects and monolayer reorganization caused by mercury.[9, 10]

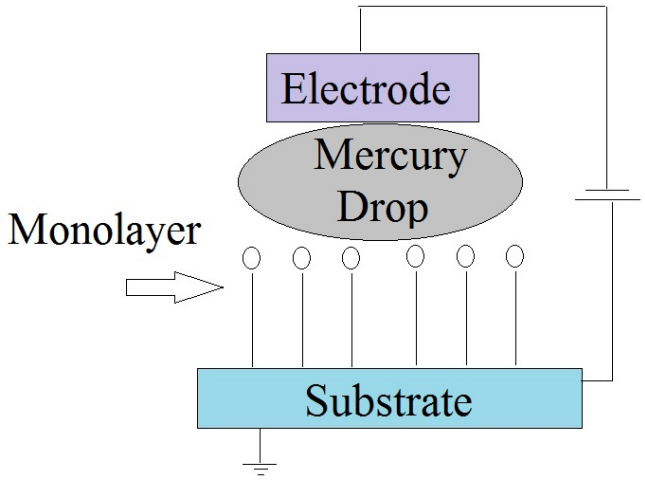


Figure 3: Basic diagram showing the mercury drop method.[9]

Section 1.4.2: Metal Deposition

This technique is one of the most invasive and damaging techniques used to fabricate a top-contact. One main problem is the formation of pinholes in the added layer and/or damage of the molecular layer during deposition.[11] This leads to the creation of an array of metallic filaments that can short circuit the device. Recent statistical data have reported that 98.8% of the 13440 devices composed of gold top-contacts deposited onto alkanethiol monolayers short short-circuited[12]. Other variations of this technique use indirect deposition, which consist of using an inert gas to collide with the incoming gold particles ultimately reducing their kinetic energy. Although, the later method is more effective the main problem with this method is the lack metallic film thickness control.[7]

Section 1.4.3: Top-Contact Deposition using a Sacrificial Substrate

In order to avoid the invasive disadvantages of the previously mentioned methods a sacrificial substrate can be used to deposit the top-contact, and then deposit the top-contact onto the desired monomolecular layer. The sacrificial substrate is first treated by one of the previously mentioned methods and once the top-contact is formed the substrate is discarded. The way that the substrate is discarded depends on the technique used. A notable technique was presented by Niskala et al.[13] In this technique nanotransfer printing with low surface energy

perfluoropolyether (PFPE) based stamps is used to form molecular junctions. In the case of this experiment the PFPE is the sacrificial substrate, which is discarded after the film has been deposited onto a SAM on a metallic thin film. [13] The main disadvantage of this procedure is the fact that the interaction between the monomolecular layer and gold must be greater than the interaction between the PFPE and gold. Furthermore, damage to the monomolecular layer could be caused if too much force is applied when attempting to transfer the top metallic layer.

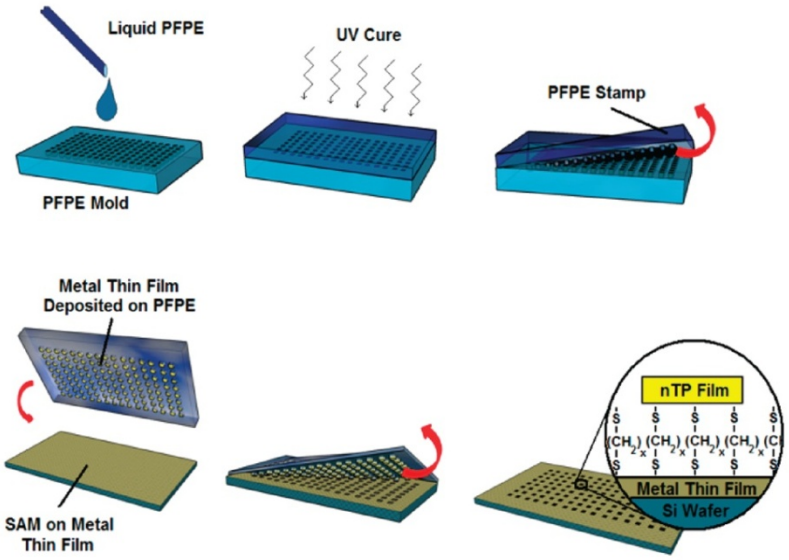


Figure 4: Scheme showing the use of a sacrificial substrate to fabricate the top-contact.

Section 1.4.4: Surface Mediated Metal Deposition (SDMD)

This method uses diffusion of the metal atoms onto a molecular monolayer attached to a conducting surface, such that there is contact with the monolayer with minimal heat transfer or structural disturbance. This is accomplished by shielding the molecules from direct exposure to the metal vapor. As reported a layer SiO_2 is used to protect the monolayer as the evaporated metal is placed onto it. It is through diffusion that the metal atoms migrate through the SiO_2 surface onto the monomolecular layer, thus forming a top-contact. Even though this method is reported to be highly efficient it still has a disadvantage. This disadvantage is that the conductance within the molecular layer is additive with a junction containing less than ten molecules in parallel. Therefore, this implies that conductance additivity does not apply for a "large number" of molecules oriented in parallel.[14]

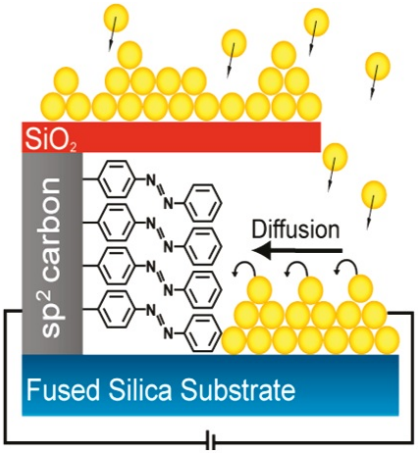


Figure 5: Schematic of SDMD technique with an azobenzene monolayer built via electrochemistry and attached to the conductive sp^2 sidewall.[14]

Section 1.4.5: Top Laminated Graphene Electrode

A method presented by Wang et al, proposes the use of graphene as a top-contact electrode. The electrode is deposited onto a SAM, which is later covered by a thin film made of gold. Graphene is used as a "soft contact" to protect the organic monolayer, made of either alkenethiols or alkenedithiols, from gold nanoparticles that can filter or damage the monomolecular layer, thus short circuiting the device. This technique has a percent output of functioning devices, equaling about 90%. The main disadvantage of this technique is that some conducting polymers (PEDOT:PSS), which are less than 2 nm long will yield a low conductance due to the nature of the interface of graphene with the polymer.[7]

Section 1.4.6: Top-Contact Deposition via Langmuir Blodgett

This method was initially presented by the research group Platon at Zaragoza University in the doctoral thesis of Dr. G. Pera. The method proposed involved the generation of metallic nanoparticles onto a monomolecular LB layer. In order to achieve this chloroauric acid ($HAuCl_4$) was dissolved in water until a $2 \cdot 10^{-5}$ M concentration was obtained. The solution was then used as the subphase onto which a amphiphilic molecules which lead to the formation of an ionized film were spread. During the transference process the metal precursor ($AuCl_4^-$) is incorporated into the monolayer to maintain the electroneutrality of the system. Once the monomolecular layer was transferred onto the bottom metallic substrate, it was irradiated with a UV lamp until gold particles were reduced to an Au(0) metallic film and act as a top electrode.[9] Although this

method does not lead to short-circuits, it is worth noting that the surface coverage of the top electrode is not complete This technique is also the base of this research, which aims to create a molecular junction in an economical and efficient way

Section 1.5: Experimental Hybrid CMOS

There has been much focus into characterization of electron transport through molecular monolayers, yet most research has not been geared towards using appropriate materials which can be compatible with conventional integrated circuit technologies.[15] That is, most research has focused in using gold as a bottom substrate material due to the straightforwardness and reliability of organic monolayers built onto gold. However using gold is not a benefit when dealing with the hybridization of technologies, this is mainly due to the nature of gold, which has propensity to form energy traps in silicon. Using gold and evaporating it to form top-contact has been shown to degrade and/or shift monolayers in junctions. Characterization of previous reported molecular electronic devices have mostly consisted of indirect contacts like STM probes or devices, which rely on "soft" top contacts (mercury drops, carbon nanotubes, or electrolytes).[15] It is important to remark that the electrical performance of the molecular monolayer is extremely dependent on the materials and characterization used.

The National Institute of Standards and Technology (NIST) has already been looking into hybrid forms molecular electronic devices based on CMOS compatible techniques. Such research is of great importance because it proves that indeed integration of these devices is possible, and enables on-chip characterization of the molecular devices by using the CMOS circuitry. One such device that was fabricated by the NIST was made using traditional very large scale integration tools to layout tools (VLSI) and CMOS fabrication.[15]

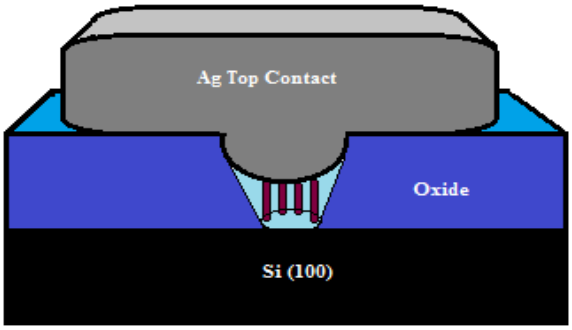


Figure 6: Cross section of a molecular electronic device. The silver top-contact is on the foundation of oxide and molecular nanowires which are depicted in the center of the oxide layer.[15]

Furthermore, research provided by NIST mentions that in order to avoid displacing the molecular monolayer, silver (Ag) was used during metal evaporation. It is reported that silver is known not to show displacement of the molecular junctions when used as a top-contact. It is important to note that to observe the electrical characteristics of the molecule it is necessary to use highly (degenerately) doped Si. This is because such material will facilitate the detection of the intrinsic molecular properties, rather than depletion in the substrate, due to the work function difference between the lightly doped bottom Si contact and the Ag top contact. Interestingly the molecules chosen for this experiment are alkanethiols. Due to quantum tunneling method of transport through such molecules it is expected that longer molecules will have a longer tunneling barrier, thus devices with longer molecules will exhibit less current.[15]

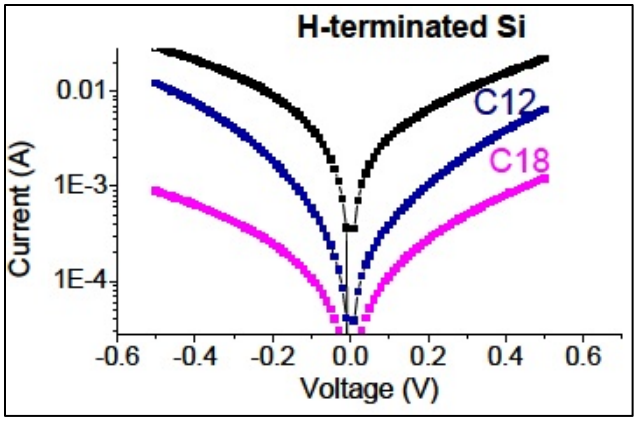


Figure 7: Results of an applied bias across the top and bottom contacts which results in the current through the junction. Here the current vs. voltage curves, from top to bottom are the curves with no organic monolayer (hydrogen terminated Si), with octadecanethiols (molecules 18 carbons long), and dodecanethiols (molecules 12 carbons long).[15]

Pascal Martin et al.[6] from the University of Paris Diderot have incorporated 5-10 nm thick organic layers based on oligothiophenes grafted onto gold electrodes incorporating diazonium electroreduction. These layers show reversible on/off electrochemical switching managed by the redox state of the oligomer. Therefore, they were determined to be of interest for solid state molecular electronic junctions. The junction fabrication was done with all CMOS technology in order to check for molecular robustness. Furthermore, the current density vs. voltage curves (*J-V)* characteristics were explored in order to determine whether quantum tunneling still remains the dominant charge transport mechanism, or if the use of these simply dopable layers can give rise to new device functionality not seen in thinner layers. Overall this experiment demonstrates the basis for hybrid organic/inorganic CMOS technology and effective construction of novel organic electrodes.

Section 1.6: Beyond the State of the Art and Objectives of this Work

As the microelectronic industry reaches the 10 nm dimensional scaling limit,[4] new nanotechnologies must merge with the heavily invested silicon based electronic components. One of the main objectives of molecular electronics is to offer an alternative solution to the current problems faced by the microelectronics industry. Being able to further downscale the dimensions of current CMOS, requires knowledge of the electronic limits of silicon based technologies, and the possible solutions that molecular electronics can offer. As it has been

presented in section 1.4 there are two methods to build molecular junctions. The most feasible method and the one presented in this report, needs an array of molecules which are anchored onto a substrate to form a monomolecular layer. A top-contact is then deposited onto the substrate to from a complete molecular device.

There are several methods which can be used to deposit a top electrode onto a molecular monolayer (see section 1.4). However, these methods have yet to be functional for industrial applications. The main problems involved when attempting to deposit a top contact onto a monolayer include, but are not limited to: filtering of the metallic nanoparticles, reorganization of the monomolecular layer due to interaction with the metallic top contact, creation of pinholes in the monolayer, lack of contact homogeneity, and short circuiting of the device.

This work attempts to create a top-contact using the principles outlined in *Section 1.4.6: Top-Contact Deposition via Langmuir Blodgett*. This method will avoid the invasive and damaging outcome of metal deposition, and will also be performed in a more economical way. The experiment also attempts to stay within the outlined points stated by NIST (see section 1.5) ; this will enable the creation of silver top-contact that could be compatible with current silicon based technologies.

Two different types of monomolecular thin films have been investigated. The first molecule chosen was behenic acid (Figure 8), abbreviated in this work as BA. Behenic acid was used as a test molecule, since it is a well-known material, economic, and because of its nature as a fatty acid which tends to form reproducible and reliable monolayers.

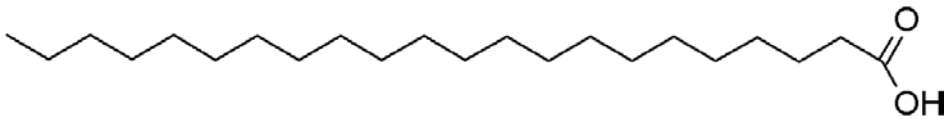


Figure 8: Chemical Structure of Behenic Acid.(BA)

The terminal acid group of this amphiphilic molecule makes it suitable for initial testing in order to observe the interaction of silver with the acid “head group”. As a side note, it is also worth noting that the purpose of using BA was to test the viability of the proposed method avoiding the the unnecessary use of the molecule of interest for the final objectives of this work, which is *a la*

carte homemade molecule and therefore a rather limited amount of material was available in our laboratory.

The experiment was performed (see Figure 9) in a similar fashion to the one presented in *Section 1.4.6: Top-Contact Deposition via Langmuir Blodgett*.

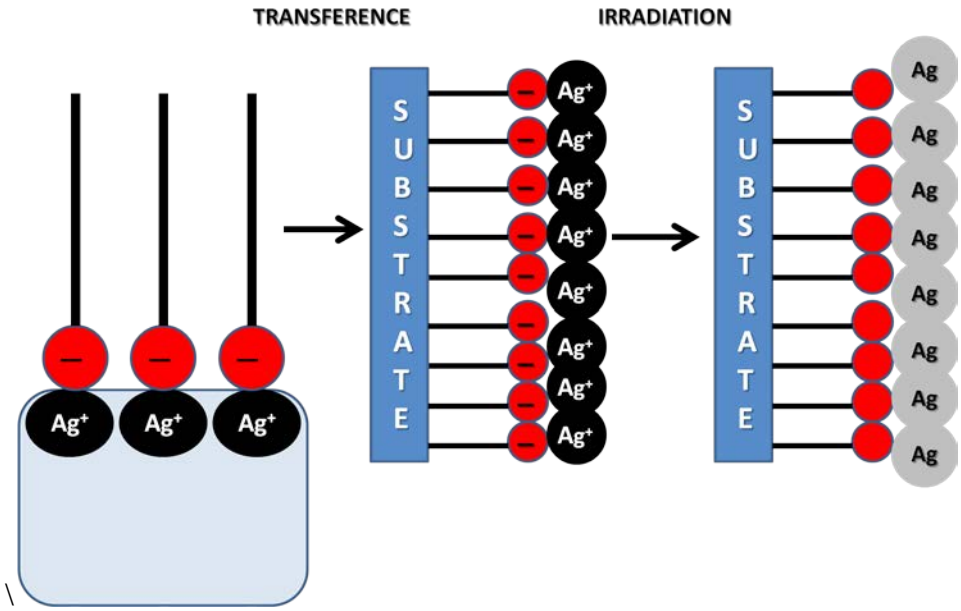


Figure 9: Scheme of the method proposed in this work for the fabrication of a metal-molecule-metal device. First, a Langmuir film of the surfactant in $AgNO_3$ is prepared. Then, the film is transferred onto a metallic substrate and subsequently irradiation of the film takes place with the reduction of Ag (I) to Ag(0).

Given that promising results were obtained with BA, the next step was the use of a highly conjugated material of interest in molecular electronics. Oligo phenylene-ethynylene oligomers (OPEs) are attractive for molecular electronics; due to their rigid π-conjugated backbone, which makes them ideal for efficient electron transport. [16-23] In addition, the delocalized π electrons, account for rapid transfer of energy and excellent luminescent properties exhibited by the OPEs.[24-27]

In particular, the material used in this work is 1,4-bis-(4-phenylethynyl)-benzene-4'-4'-bis(carboxylic acid) which is abbreviated in this work as OPE2A (Figure 10).

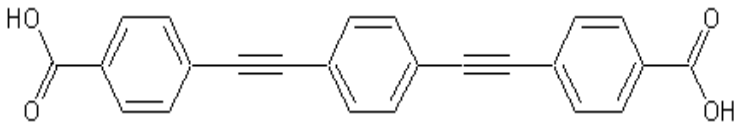


Figure 10: Chemical Structure of1,4-bis-(4-phenylethynyl)-benzene-4'-4'-bis(carboxylic acid) abbreviated in this work as OPE2A

This compound has been studied before in Langmuir-Blodgett films by the research group Platon previously.[41] Interestingly, it was demonstrated that the pH of the sub-phase used for the films fabrication has a significant influence in the conductance of the film. Therefore, the counter ion present in the subphase could also have a crucial role in the electrical properties of the film. This result together with the promising conclusions presented later in this work for the use of the LB method in the fabrication of the top-contact electrodes are the main reasons why this molecule was used to fabricate metal-molecule-metal devices in this project.

The silver top-contact in the OPE2A monolayers was deposited using a similar procedure as described before for BA (Figure 9).

In addition, a slightly different approach for the fabrication of the top-contact electrode is presented in Figure 11. In this case, a Langmuir film of OPE2A was prepared onto a water subphase. The film was transferred onto a solid substrate and an aqueous solution of $AgNO_3$ was deposited on top of the organic film with the aid of a pipette. Subsequently, the film with the silver solution was irradiated, which lead to the photoreduction of Ag (I) to Ag(0) and the formation of a top-contact electrode.

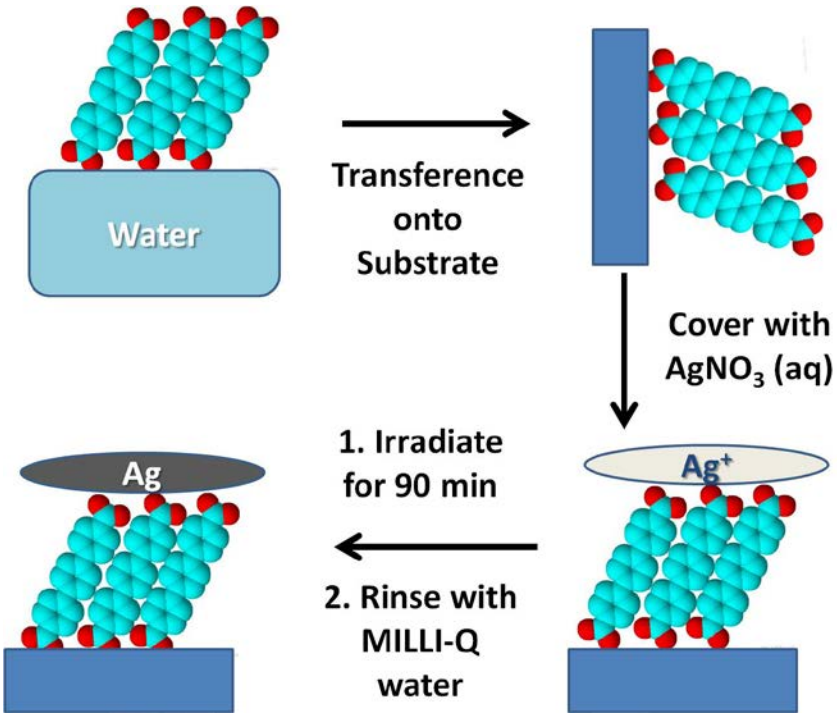


Figure 11: Basic diagram illustrating the overall experimental set up for creating a silver top-contact onto an OPE2A monomolecular film.

Chapter 2: Experimental Section

In this chapter the compounds used to fabricate the molecular devices will be presented, as well as the reasons for choosing these materials. The facilities used to fabricate the devices will be described and the overall working principle discussed. Experimental details regarding the concentration, grade, supplier, etc. are gathered in Table I. The type of substrates used for each characterization technique, are presented in Table II

Section 2.1: Materials

Behenic acid is a fatty acid molecule with C-C and C-H single σ-bonds and, does not contain conjugated π orbitals apart from those in the functional terminal group. The carboxylic acid is a polar group that permits the anchoring of the molecule at the water surface and provides stability to the Langmuir film. In addition, the hydrocarbon chain of this molecule exhibit significant van der Waals forces between neighbor molecules, thus generating very stable

monomolecular layers.[28] These characteristics of behenic acid made it alluring for initial testing. Since this method, photoreduction of a metal precursor, had been successfully used by the Platon Research group before,[29] the challenge here was the use of a cheaper and also efficient metal electrode, e.g. the use of silver instead of gold. Incorporation of a cation metal precursor requires the formation of negatively ionized monolayers and that is the reason why we used a carboxylic acid.

When the behenic acid is spread onto the silver nitrate $AgNO_3$ aqueous subphase, the hydrophilic part of the molecule is initially ionized into COO^- and H^+. To maintain the electroneutrality of the system, the majoritary cation in the subphase, i.e. Ag (I) will interact with COO^- forming a double ionic layer.

In order to orient the hydrophilic group in an outward position (see Figure 8), the substrates, i.e. quartz and glass for the characterization experiments, were initially treated with hexamethyldisilazane. This makes the substrate highly hydrophobic, thus the hydrophobic part of the molecule, i.e. the hydrocarbon chain, will be attracted to it (Figure 9). Once the monomolecular layer with silver cations is transferred onto the substrate it is irradiated with UV light (254 nm) for different periods of time. It is at this moment that the photosensitive nature of the silver plays an important role, as it changes oxidation state from +1 to 0 (Equation 2).

$$Ag\,(I) + e^- \longrightarrow Ag_{(s)} \qquad (2)$$

In this wok an OPE derivative labeled as OPE2A (figure 10) was assembled into Langmuir-Blodgett film to fabricate a metal-monolayer-metal device. Two different approaches were followed to fabricate the top-contact electrode:

i) Langmuir films of OPE2A were prepared onto a concentration 10^{-3} M $AgNO_3$ aqueous subphase and then transferred onto a conducting substrate (for research purposes other substrates were also used to permit the characterization of the organic film). The films were irradiated (256 nm) to induce the photoreduction of Ag (I) generating a silver metallic film on top of the organic monolayer.

ii) Langmuir films of OPE2A were prepared onto a pure water subphase and transferred onto a conducting substrate. Then a concentration 10^{-2}M AgNO3 aqueous solution was deposited on top of the film and irradiated (256 nm) to

induce the photoreduction of Ag (I) generating a silver metallic film on top of the organic monolayer. The substrate was subsequently rinsed with Milli-Q water.

Table I : The materials used are listed including the experimental concentration of BA and OPE2A. * Silver Concentrations differ in BA and OPE2A experiments. The concentrations will be given in section 2.2.

Compound	**Grade (%)**	**Molecular Weight (g/mol)**	**Supplier**
Behenic Acid (BA)	99	340.58	Sigma-Aldrich
1,4-bis-(4-phenylethynyl)-benzene-4'-4'-bis(carboxylic acid) (OPE2A)	99	318.32	University of Durham /Designed and synthesized a la carte for project CTQ 2009-13024
Silver Nitrate ($AgNO_3$)	99	169.87	Sigma-Aldrich
Hexamethyldisilane	99	161.39	Sigma-Aldrich
Chloroform	99	119.38	Sigma-Aldrich
Acetone	99	58.08	Panreac
Milli-Q H_2O	NA	18	Distillator Faculty of Science

Table II: Type of Substrate, cleaning method, technique used and equipment brand used to characterize the films deposited onto the distinctive substrates.

Substrate	**Cleaning Method**	**Use for Characterization Technique**	**Equipment Brand**
Quartz	Ethanol/acetone & Hexamethyldisilane	UV-vis	Varian Cary 50 Bio UV-vis
Glass	ethanol/acetone	SEM	FEI™ series Quanta™ 250
Mica	Cleaved with cello tape	AFM	Multimode 8 Veeco with silicon tip of brand Bruker (*f*= 300kHz, *k*= 40mN
Gold	Rinsed with ethanol	XPS	Kratos AXIS DLD

Section 2.2: Fabrication of Langmuir and Langmuir Blodgett Films

Some notable problems in molecular electronics arise due to the non-reproducible quality and/or structure in the devices' molecular monolayers.[30] Thus, solution casting methods are appealing for industrial large transfer processing; however, these methods present the disadvantage of preventing precise control over the molecular layer architecture and arrangement. Self-assembly methods have been probed to produce molecular monolayers of functionalized molecules on a wide range of surfaces, with the assembly of thiols on gold being particularly common and giving rise to excellent quality films formed by the strong gold-sulfur linkage.[31-35] However, certain limitations in the self-assembled methodologies have been described in the literature, including the tendency of organic thiols to oxidize to disulfides,[30-34] or a rather fluxional gold-sulfur bond which leads to dynamic switching of the molecular conductance observed in conductance studies.[37-39] Using a monolayer assembly technique such as Langmuir Blodgett will allow the user an acceptable degree of control when forming a molecular film as thin as one molecule. For this reason the Langmuir Blodgett technique is of

particular interest for this research, since it is possible to obtain a good degree of control of monolayer formation. In addition, in the LB methods films can be either chemi or physisorbed in the substrate which also broadens the number of metal-organic interfaces that can be studied. Finally, another important reason to use the LB method in this work is the possibility of incorporating a metal precursor from the subphase to fabricate the top-contact layer.

LB films are prepared in instruments called Langmuir troughs. Troughs are frequently made of Teflon®, which is inert and hydrophobic, thus it will not contaminate the aqueous subphase that fills the trough. In the case of this experiment a medium and a mini KSV-NIMA troughs were used. Figure 12 shows a photograph of the medium KSV-NIMA trough used in this work.

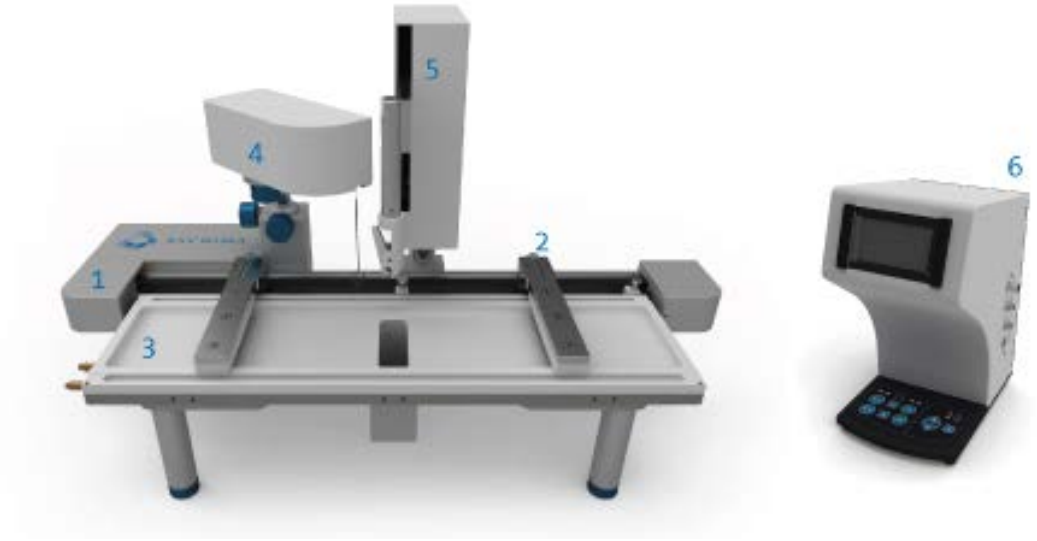


Figure 12: Photograph of the NIMA-KSV through used in this work. 1) Frame; 2) barriers; 3) trough top; 4) surface pressure sensor; 5) dipper; 6) interface unit.[40]

The trough is filled with an aqueous subphase until a convex meniscus is formed. In the case of this work Milli-Q water and $AgNO_3$ (aq) subphases were used. After the trough is filled a solution containing the molecules with which the monolayer will be fabricated, which are typically amphiphiles, is spread drop by drop using a Hamilton syringe onto the subphase.

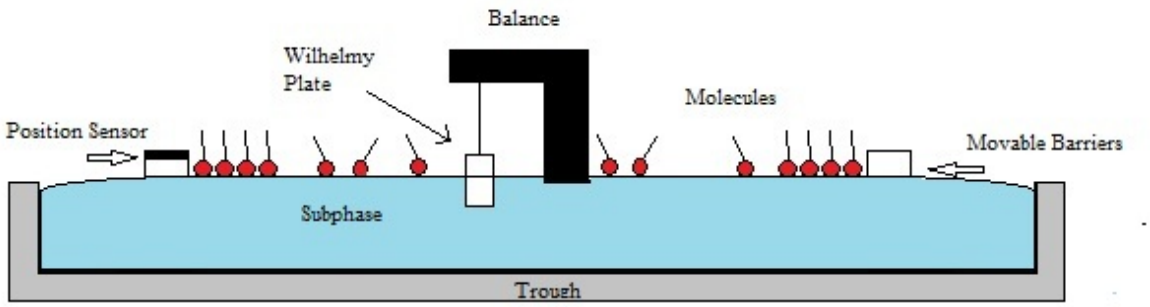


Figure 13: Scheme of a compression in order to make a Langmuir film.

Once the solvent has evaporated of the surface the molecules are compressed by a pair of evenly placed Teflon barriers (see Figure 13), which do so at a constant rate. During the compression process the surface pressure is determined (see Equation 1) with the use of sensor known as the Wilhelmy Plate, and another sensor is used to determine precisely the barrier position in order to calculate the area per molecule. The end result is the surface pressure-area per molecule (π-A) isotherm (see Figure 6).

$$\pi = \gamma_{clean\ surface} - \gamma_{surface\ plus\ monolayer} \quad (3)$$

There are many factors that affect the number, type of phases, and phase transitions an isotherm goes through. Some of these factors rely on the temperature, compression speed, pH, presence of salts, etc.[28] Figure 14 represents an example of a generic isotherm exhibiting transitions ranging from gas to solid. If the area per molecule is large enough, then the Langmuir film will be present in a bi-dimensional gas phase **(G).** In this phase the molecules of the surfactant are not interacting. As the monolayer is compressed the surface pressure elevates signaling the presence of a very compressible liquid state. During this state the molecules experience attractive forces with enough intensity to form a more compact structure, thereby forming the liquid expanded **(LE)** phase. A further reduction of the area per molecule gives way to a less compressible but more ordered phase known as the liquid condensed **(LC).** The organization of the monolayer is compact and the hydrophobic part of the molecules is oriented more perpendicular with respect to the interface. Continuing the compression of the monolayer and before the collapse the solid phase **(S)** is reached. In this phase the monolayer is rigid and the hydrophobic chains form a compact structure. If pressure continues to increase the monolayer

collapses due to an excess of the minimum value of physical area occupied by the molecule. The rupture of the monolayer can lead to the formation of multilayers or a loss of surfactant material into the subphase.[7]

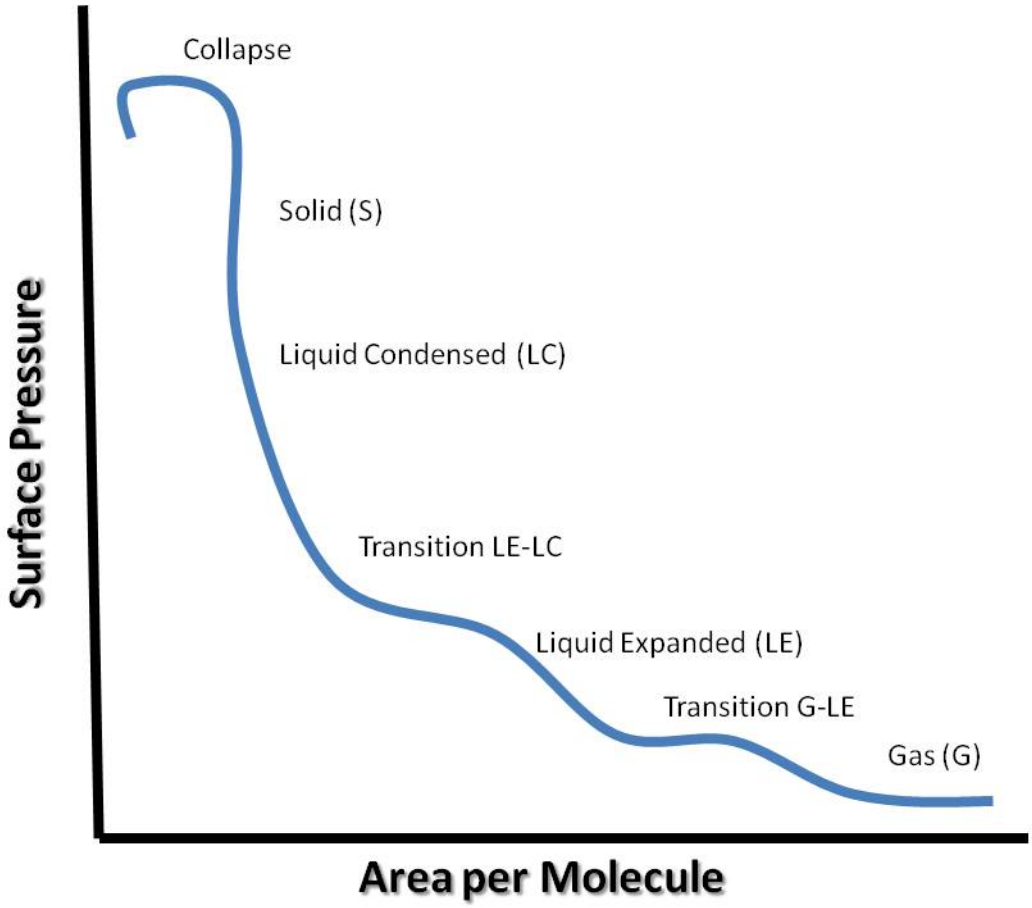


Figure 14: Typical surface pressure vs. area per molecule isotherm. Depending on the material and preparation conditions, not all the isotherms show all the phases and phase transitions here indicated.

Once the closed packed monolayer is formed it can be transferred mechanically onto a solid substrate (see Table II), so long as it is submerged and withdrawn at a constant rate going through the aqueous surface. There are different ways of molecular orientation; depending on the nature of the substrate, the molecules can either orient “heads” or “tails” in the outward position.

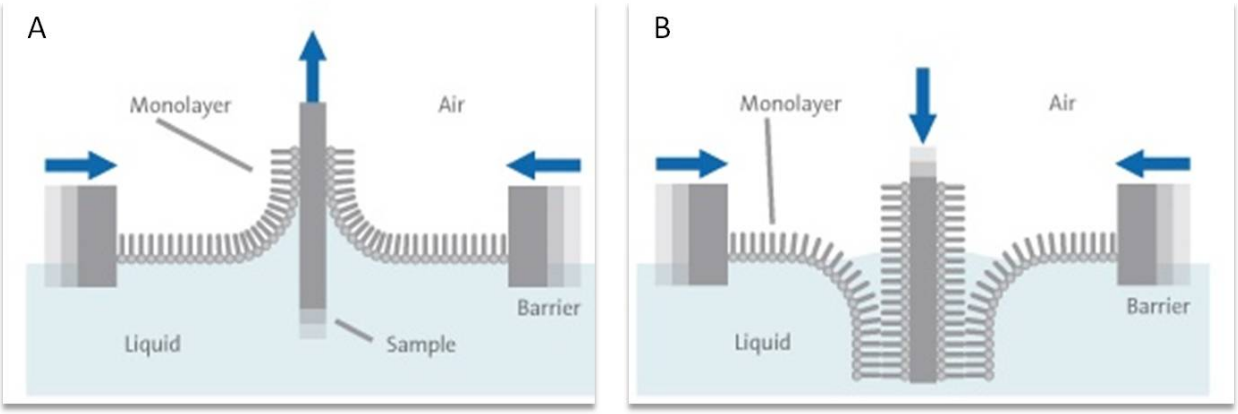


Figure 15Scheme of a Langmuir Blodgett transference process onto: A) hydrophilic substrate, and B) hydrophobic substrate. [40]

The thickness of the layer is controlled by the number of dips that the substrate is subject to, and a first indication of the quality of the deposition is given by the transfer ratio, which is defined as the ratio of the decrease in Langmuir monolayer surface area divided by the area of the solid support being coated. There are different types of transferences (see Figure 16) depending on the nature of the organic material and the substrate.

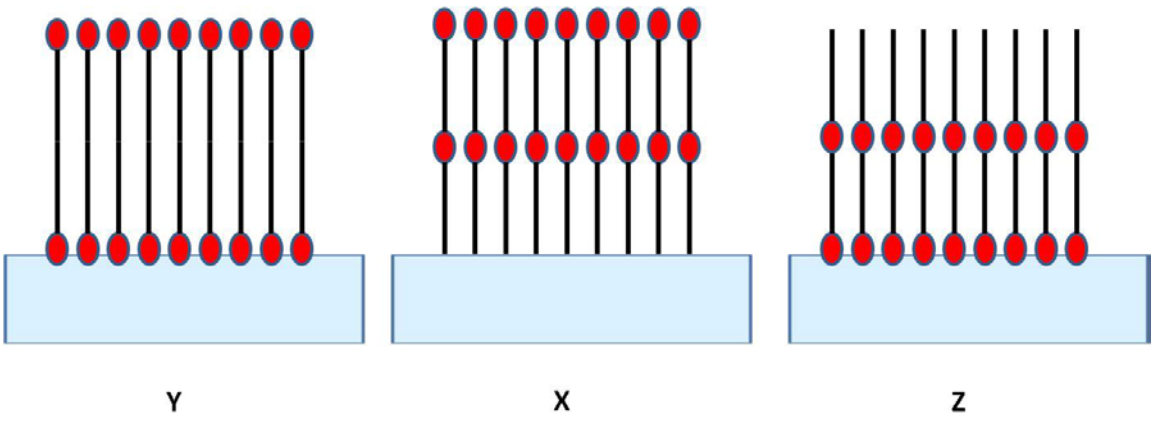


Figure 16: Three different Langmuir Blodgett transference types. [9]

Section 2.3: Characterization of Langmuir Blodgett Films

In this section the equipment used to characterize the films and the top-contat electrode will be presented and their overall working principle will be briefly discussed. Refer to Table II for information regarding the substrate used and the brand of the instrument used for each characterization.

Section 2.3.1: UV-Vis Spectroscopy

Ultraviolet-visible spectroscopy (UV-vis) uses light in the ultraviolet-visible range in order to determine the absorbance of a species in solution. The method is described is mathematically described by Beer-Lambert's law.

$$A = log_{10}\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot l \quad (4)$$

In equation 4, A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, ε is a constant known as the molar absorptivity, c is the concentration of the absorbing species in the solution, and l is the path length through the sample.

Easily excited electrons signal a lower energy gap between the HOMO and LUMO. Since OPE2A contains π-electrons it can absorb energy in the form of UV-vis light, thus this spectroscopic technique is used in a quantitative way to determine concentration of OPE2A solution. [7] It was also used to determine the presence of the silver plasmon to probe the presence of metal silver in the films after the irradiation process. Figure 17 shows a photograph of the Varian Cary spectrophotometer used in this work.

Figure 17: UV-vis spectrophotometer and sample holder with quartz cuvette

Section 2.3.2: Scanning Electron Microscopy

The scanning electron microscope (SEM) is an electron microscope that produces images by scanning a sample with a focused electron beam. The electron gun which is located in the upper part of the microscopes column generates an electron beam of about 1nm in diameter. The beam interacts with the electrons of the atoms in the sample, creating two different types of electron signals. The first type comes from secondary electrons, which provide information about the topography of the sample. This scheme is adequate to measure the size and morphology of the particles. The second type comes from the backscattered electrons, which provide additional information regarding the heterogeneous chemical composition of the sample when comparing them with the secondary electrons.[9]

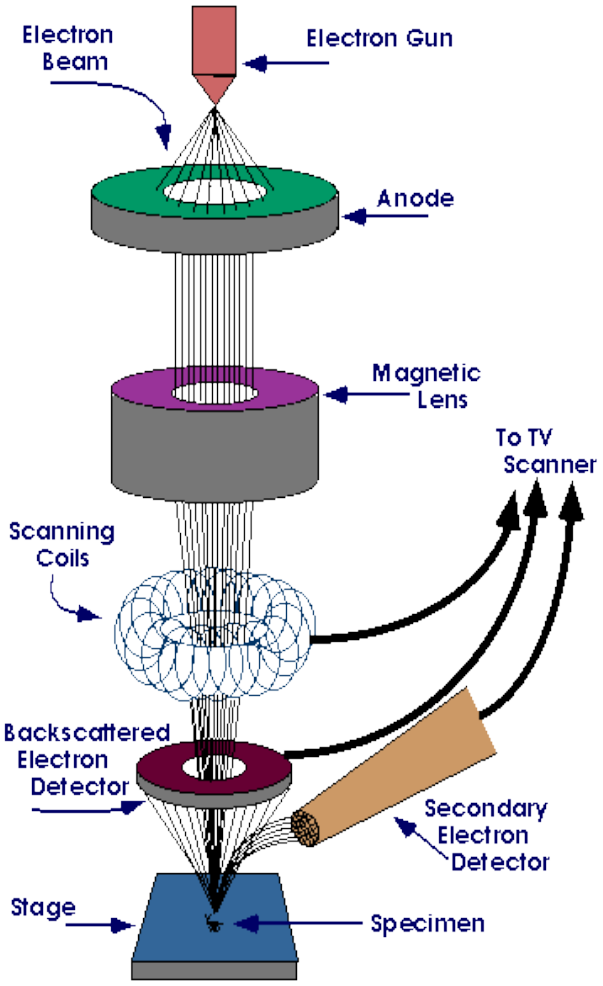


Figure 18: Scheme of the components of a SEM.[41]

Section 2.3.3: Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a type of scanning probe microscopy, which generates images by taking advantage of the attractive and repulsive forces that exist between the material and the AFM tip. The AFM tip is typically made of silicon or silicon nitride. The radius of curvature is generally in the order of nanometers. When the tip is within a close range to the sample van der Waals, capillary, chemical bonding, electrostatic, magnetic, Casimir, and

solvation forces lead to a deflection in the cantilever according to Hooke's Law. AFM experiments have been used in this work to analyze the topography of the samples.

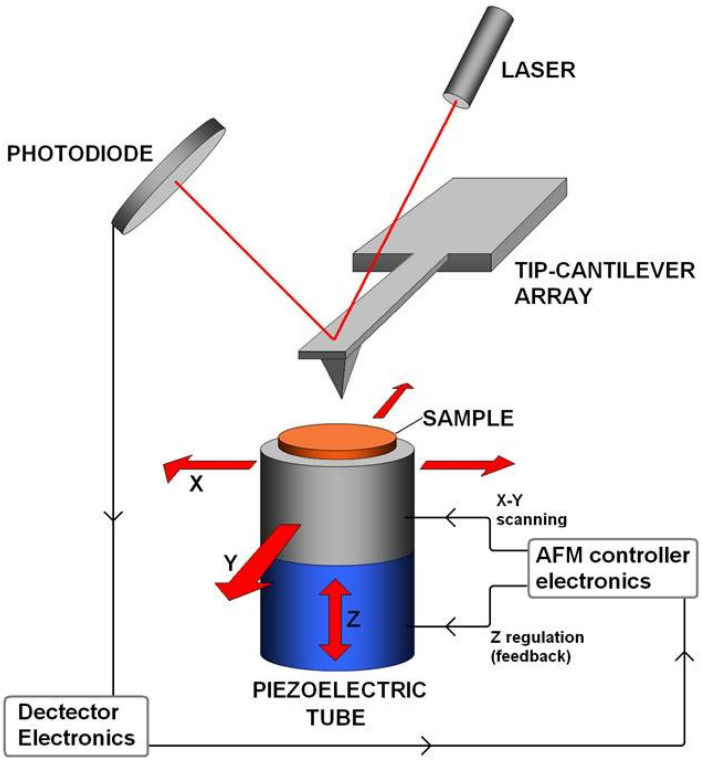


Figure 19: Basic scheme of an AFM.

Section 2.3.4: X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that uses a beam of monochromatic and non-monochromatic X-rays emitted from an aluminum Kα (1486.6 eV) or magnesium lamp (1253 eV) respectively. The sample is irradiated with the X-rays allowing the electrons to escape from the top 1 to 10 nm of the materials being analyzed.(see figure 20) The number of electrons detected per unit time versus the binding energy of the electrons detected, directly signal the identity of each element that exist on the surface of the sample. The peaks shown in the spectra are characteristic of each elements binding energy and correspond to electronic configuration of the electrons within the atoms e.g., 1s, 2s, 2p, 3s, etc. The XPS used for this experiment used a monochromatic Al Kα lamp.[9] In this project we benefit from XPS experiments to unequivocally demonstrate the presence of Ag (0) on the films.

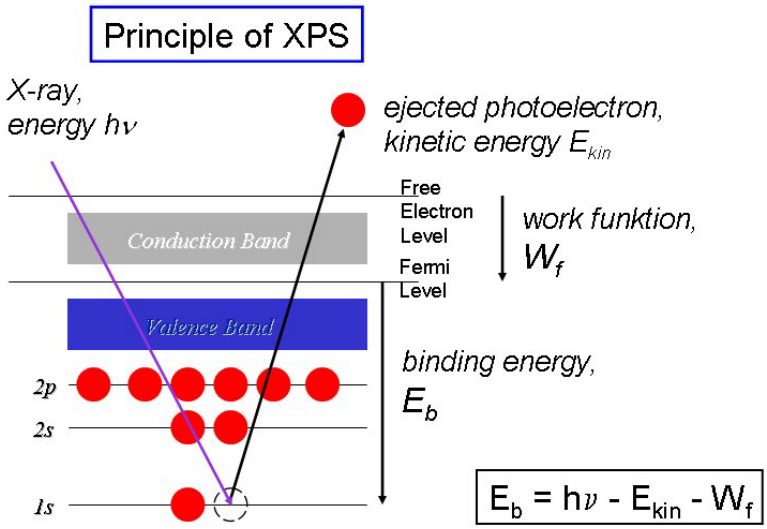


Figure 20: Scheme presenting the overall principle of XPS.[42]

Section 2.3.5: Surface Potential

. The surface potential sensor measures the potential difference above and below a thin film, and is sensitive to the sum of all the individual dipole moments. The changes in the potential difference are calculated by detecting the potential distinction between the vibrating plate which is positioned above the monolayer and the counter electrode which is immersed in the subphase underneath the monolayer. This technique is capable of determining effective dipole moments, molecular orientation, film electronic structure characterization, molecular structure characterization, and complex formation monitoring. For this experiment the potential of BA and OPE2A in Milli-Q water and $AgNO_3$ (aq) was measured using a KSV NIMA SPOT (see Figure 21).[43]

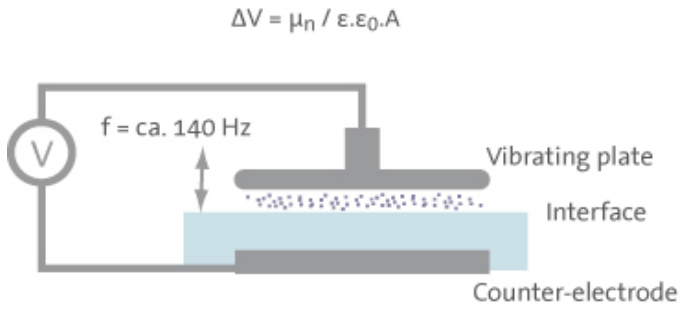


Figure 21: Surface potential measurer, with its representative interactive parts.[43]

Section 2.3.6: Brewster Angle Microscopy

Brewster angle microscopy (BAM) uses a *p*-polarized beam which is oriented towards an air-water interface. No reflection occurs at a certain incident angle, called the the Brewster Angle as determined by equation 5.

$$\tan \propto = n_1/n_2 \tag{5}$$

The Brewster angle for an air-water interface is 53°, thus under this condition the image of a pure water surface appears black. In the presence of an organic monolayer, the local refractive index changes (RI), therefore a certain amount of light is reflected and displayed as an image by the BAM (see Figure 22) . The image displayed is characterized by regions of varying brightness determined by the particular molecules and packing densities across the sampling area.[44]

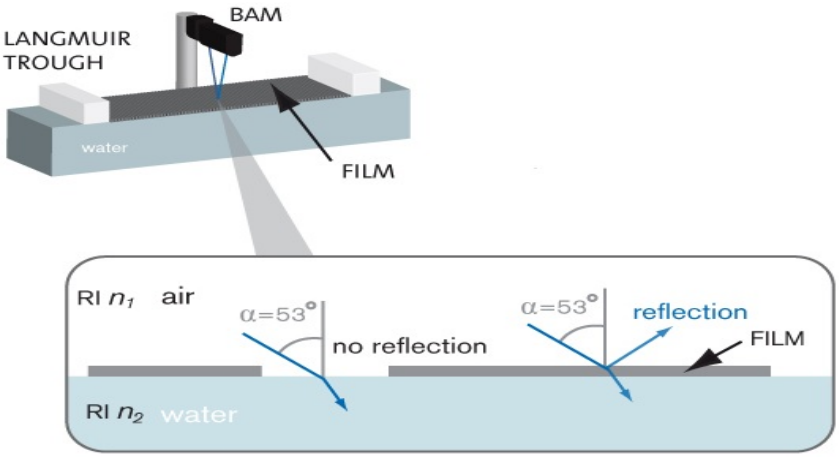


Figure 22: Scheme of Brewster Angle Microscopy. [44]

Chapter 3: Results and Discussion

In this section the preparation of Langmuir Blodgett films and their characterization techniques will be presented and explained. Please refer to the experimental section as well as to Table I and II for information regarding solution concentration, substrates used, and model of equipment.

Section 3.1: Behenic Acid

Behenic acid was chosen due to its high degree of film reproducibility, high literature background, low price, and chemical structure, but most importantly behenic acid was chosen to investigate the interaction of Ag (I) with the carboxylic acid.

The isotherm of BA is presented in Figure 23. The compression initiates a lift-off after passing the 0.3 nm^2 area per molecule mark and initiates a collapse at around 0.2 nm^2 per molecule.

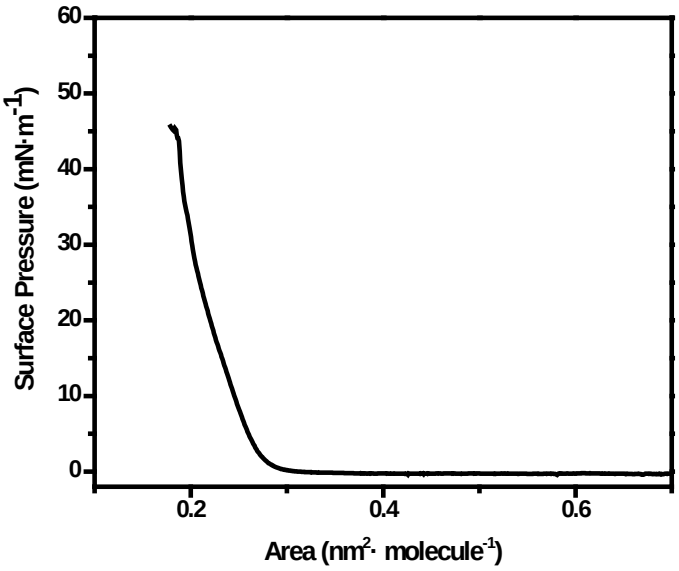


Figure 23: Isotherm of surface pressure vs. area per molecule of BA on an aqueous subphase.

To provide further insight into the film characteristics BAM images were obtained upon the compression process. As can be seen no evidences of three dimensional aggregates or microcrystals are present at the beginning of the compression process. An increase in the brightness of the images upon the compression process is indicative of a higher surface density and an increase in the tilt angle of the molecules with respect to the water surface. At a surface pressure of 52 $mN \cdot m^{-1}$ an apparent fracture of the solid phase of the film indicative of 3-D aggregate formation is consistent with a collapse of the monolayer. This collapse can be confirmed by viewing Figure 23 as a sudden decrease in surface pressure of the π-A isotherm occurs at 52 $mN \cdot m^{-1}$.

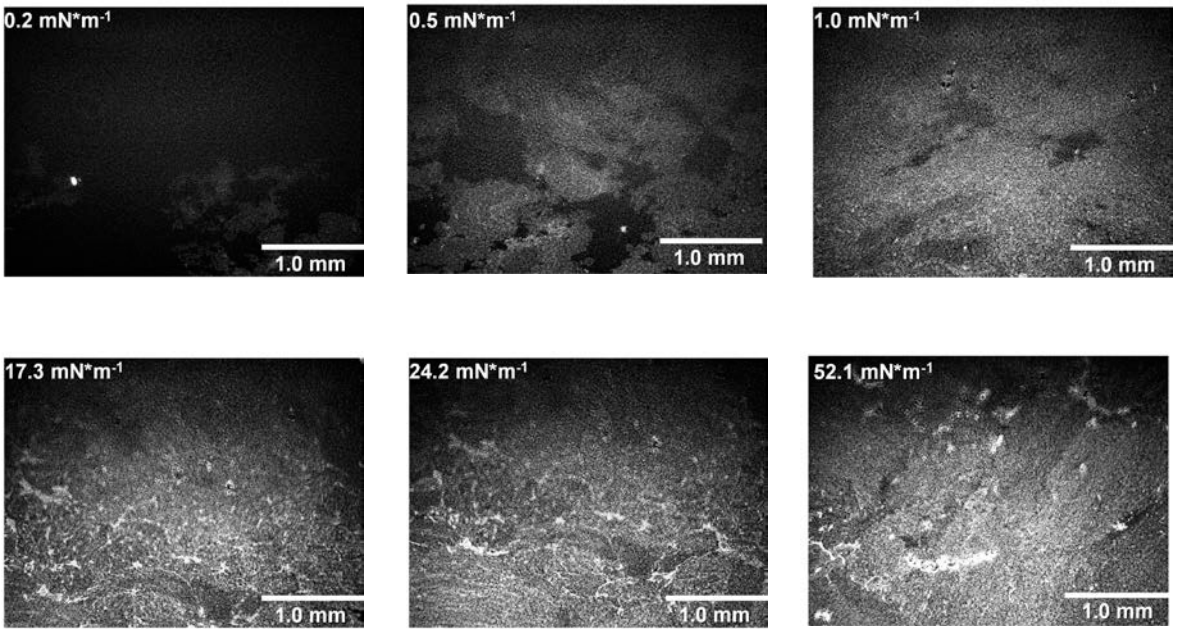


Figure 24: BAM images of BA deposited onto a silver aqueous subphase.

BA monolayers prepared onto an AgNO3 aqueous solution were transferred at a surface pressure of 20 $mN \cdot m^{-1}$ onto quartz substrates. The substrates were first incubated for 24 hours in hexamethyldisilazane to make the substrate more hydrophobic and thus assure that the “tail” of the fatty acid interacted with the hydrophobic substrate. Films were transferred during the immersion of the substrate 2 $mm \cdot min^{-1}$ with a transfer ratio of 1.

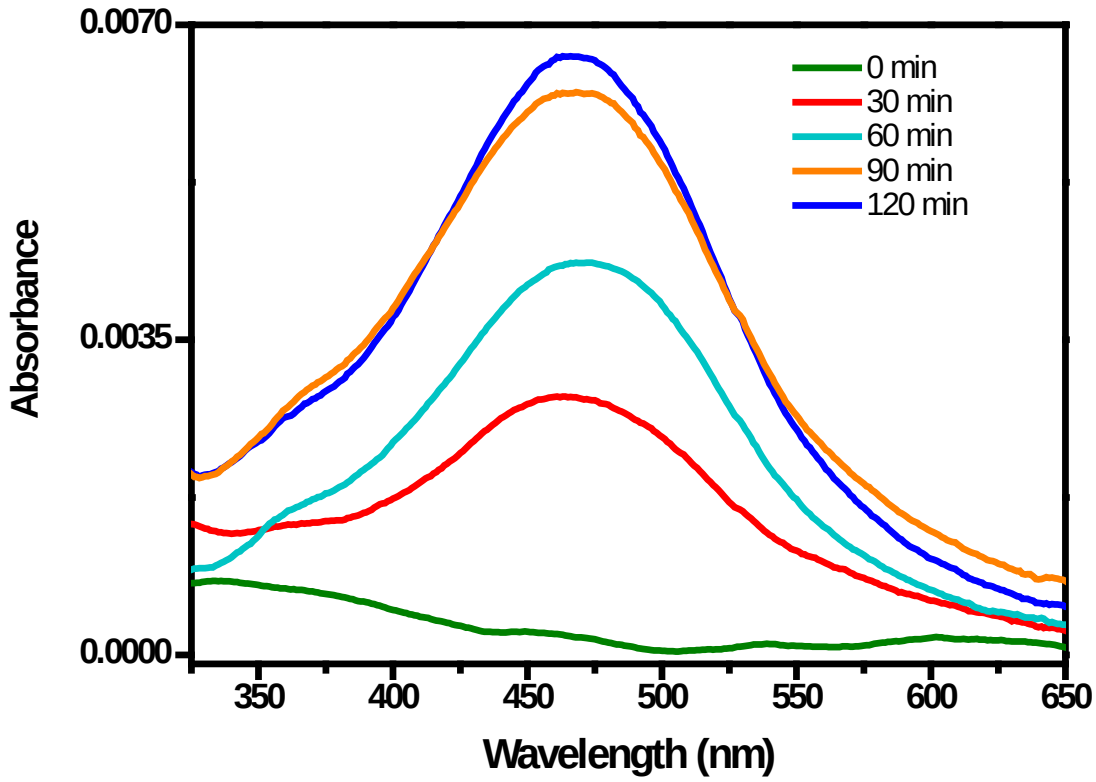


Figure 25: UV-vis spectra of a BA monolayer transferred from a 10^{-3}M AgNO3 solution before and after irradiation with a UV lamp (256 nm) for the indicated time intervals.

The first important conclusion that can be inferred from Figure 25 is the appearance of a band in the 425 nm region which is consistent with the silver plasmon. This result indicates that silver cations are being reduced to metal silver by a photoreduction process. The optimum and efficient time of irradiation was set at 90 minutes since little increase in absorbance is observed after 120 minutes of irradiation and no change noted past the 120 min time frame.

A set of experiments were performed in order to see if a lower concentration of silver cations in the subphase could also lead to the formation of a top-contact electrode. Thus, SEM images were taken using different concentrations of $AgNO_3$ in the subphase in order to determine the most efficient and inexpensive amount of silver concentration needed to obtain a homogeneous silver coverage. As can be seen in Figure 25, a $2.6 \cdot 10^{-6}$ M concentration of $AgNO_3$ in the subphase shows no evidence of formation of silver nanoparticles (NPs), clusters, etc.

However, for a 10^{-4} M $AgNO_3$ aqueous subphase SEM images are indicative of the presence of silver nanoparticles. However, large areas in the image are not apparently covered by silver NPs, i.e., a low coverage is obtained. In contrast, the use of a 10^{-3} M $AgNO_3$ subphase results in SEM images where many small Ag NPs cover the organic layer and a certain number of larger NPs or clusters can also be seen.

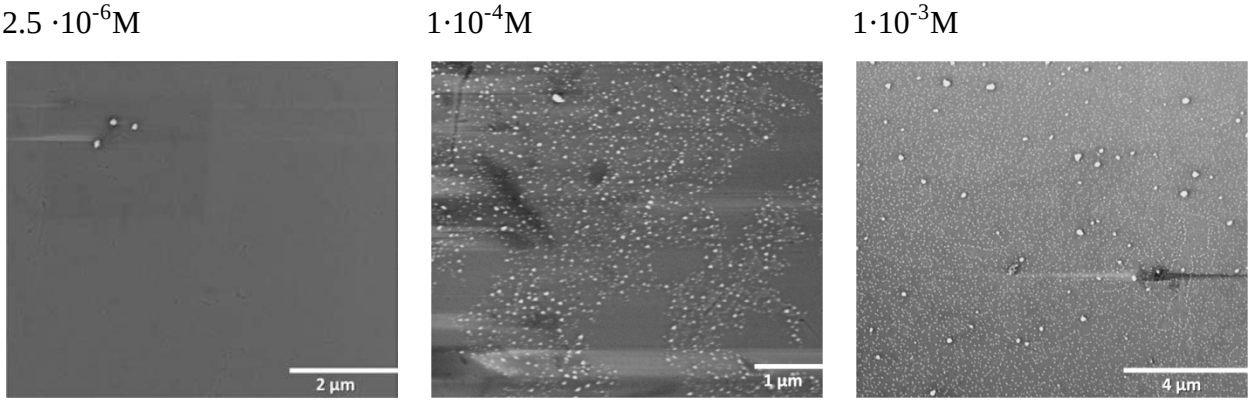


Figure 26: SEM images of BA monolayers transferred on quartz substrates from subphases of different silver concentrations as indicated in the images. The films were irradiated (256 nm) for 90 minutes .

XPS measurements were taken to further confirm the presence of Ag (0) after the irradiation of the film. Figure 28 shows the XPS spectra for an irradiated film of BA transferred from a 10^{-3} M $AgNO_3$ solution. Two peaks at 367.7 and 373.8 eV can be clearly observed, which are consistent with the presence of Ag (0) according to the literature.[45]

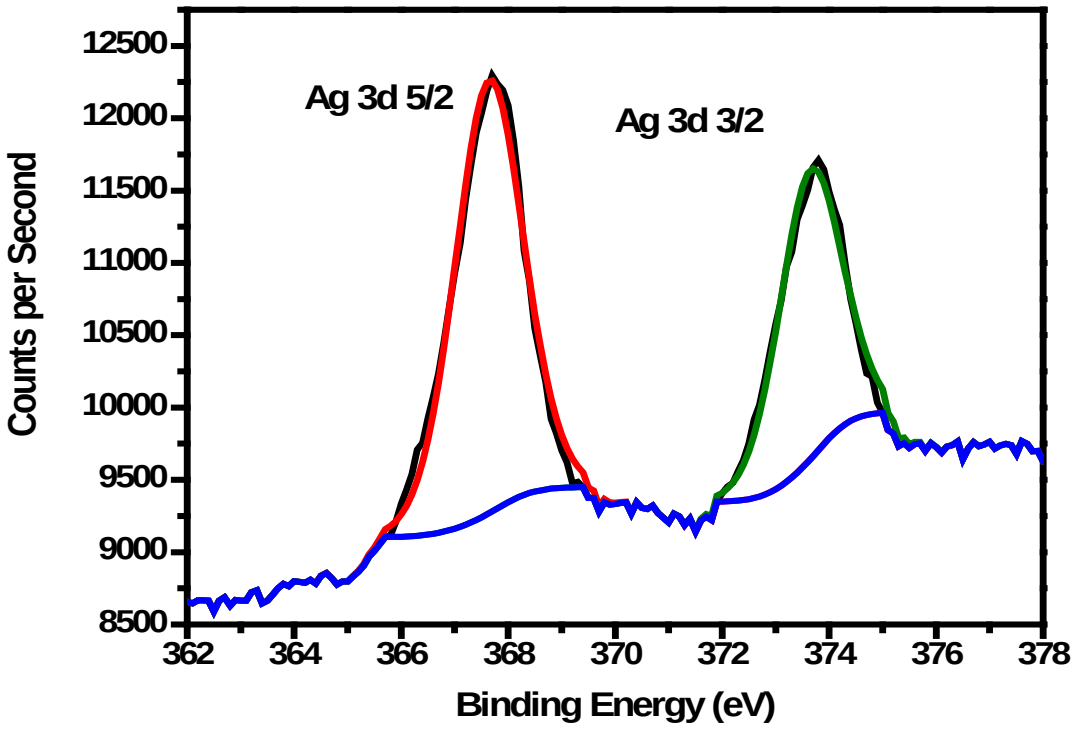


Figure 27: : XPS spectra of Ag3d for a monomolecular BA film transferred from a 10^{-3} M $AgNO_3$ aqueous subphase and irradiated at 256 nm for 90 minutes

Section 3.1.1: Conclusions of BA

Well-defined homogeneous Langmuir films of behenic acid onto water and a $AgNO_3$ aqueous subphase can be fabricated. Films of BA onto an $AgNO_3$ aqueous subphase were transferred at a surface pressure of 20 $mN \cdot m^{-1}$ with a transfer ratio of 1. After the transference process the films were irradiated with ultraviolet light (256 nm) for 90 minutes exhibiting a characteristic silver plasmon which indicated that a photoreduction of the silver cations incorporated in the film takes place. XPS also confirmed the presence of Ag (0) and SEM images of these films showed the presence of Ag NPs homogeneously distributed onto the surface.

These results demonstrate that a top contact electrode could be generated by photoreduction of a metal precursor. After this positive evidence, a material of high interest in

molecular electronics was used for the fabrication of metal-molecule-metal devices as described in the following section.

Section 3.2: OPE2A

According to previous studies of this material at the air-water interface, [25] the concentration of OPE2A used for the fabrication of Langmuir and Langmuir-Blodgett films in this work is $1 \cdot 10^{-5}$ M. At this very low concentration no aggregation of the material occurs.

The π-*A* and ΔV-*A* isotherms of OPE2A Langmuir films are shown in Figure 28. It is well-known that surface potential vs. area per molecule isotherms can detect phase changes a few square Ångstroms before they can be detected in the surface pressure vs. area per molecule isotherm. Thus, in the ΔV-*A* isotherm a slow increase of ΔV values is noted almost at the start of the isotherm. This is indicative of progressive molecular orientation, which occurs even during the gas phase when the surface pressure tends to zero.[7] No large changes in the π-*A* can be observed apart from a small expansion of the monolayer in the presence of $AgNO_3$ in the subphase. This result indicates that silver cations are adsorbed beneath the OPE2A monolayer due to electrostatic interactions. In a similar fashion, the slightly smaller values of the surface potential for the isotherm recorded onto an aqueous $AgNO_3$ subphase at a certain area per molecule indicates a better charge compensation of the OPE2A monolayer, which is in agreement with the formation of a double ionic layer.[21, 26]

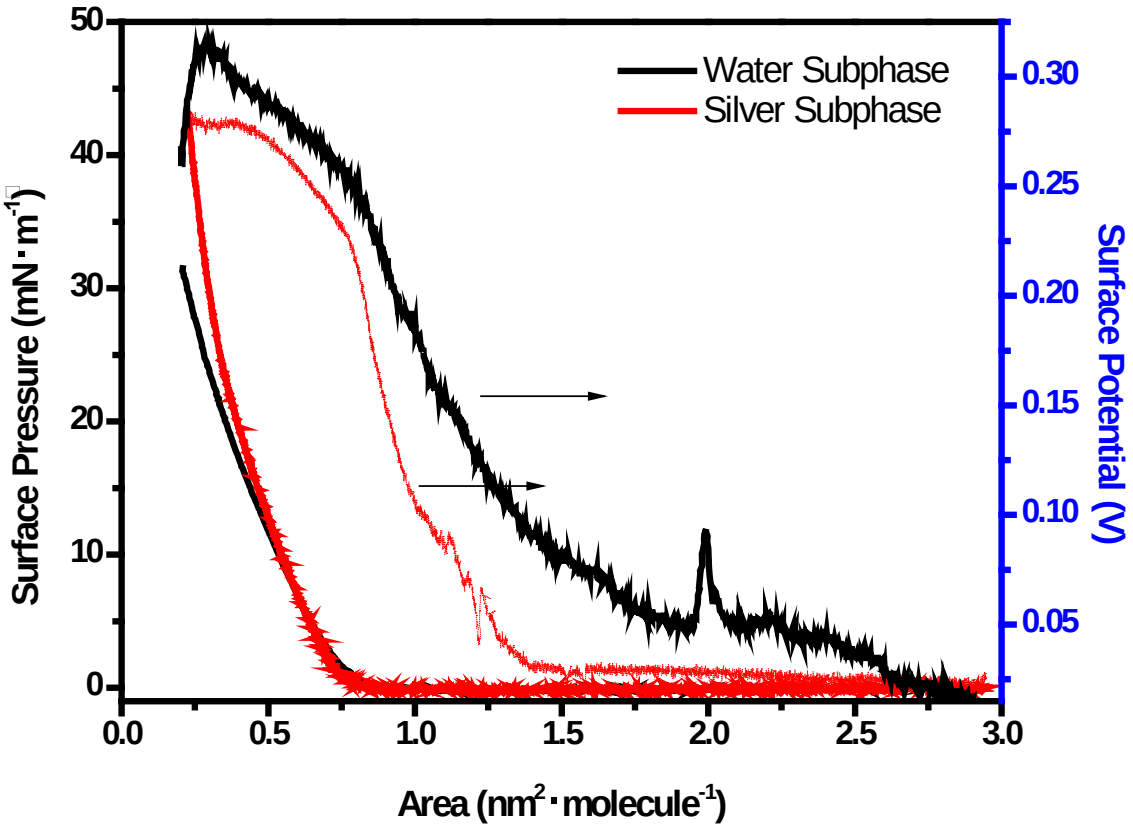
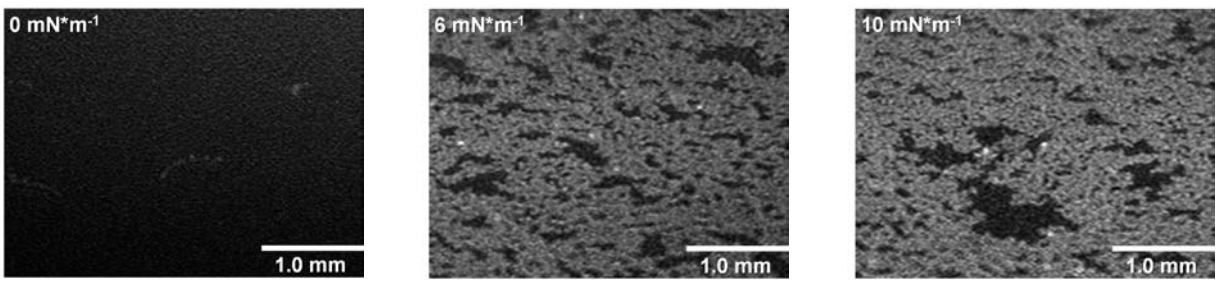


Figure 28: Surface potential and surface pressure vs. area per molecule isotherms of OPE2A onto the indicated subphases recorded at 20 ºC.

A morphological study of the monolayer at the air-water interface was performed by obtaining BAM images upon the compressing process. Figure 29 shows the BAM images recorded for OPE2A onto a pure water subphase and Figure 30 shows the BAM images recorded for an OPE2A monolayer prepared onto an $AgNO_3$ aqueous subphase.



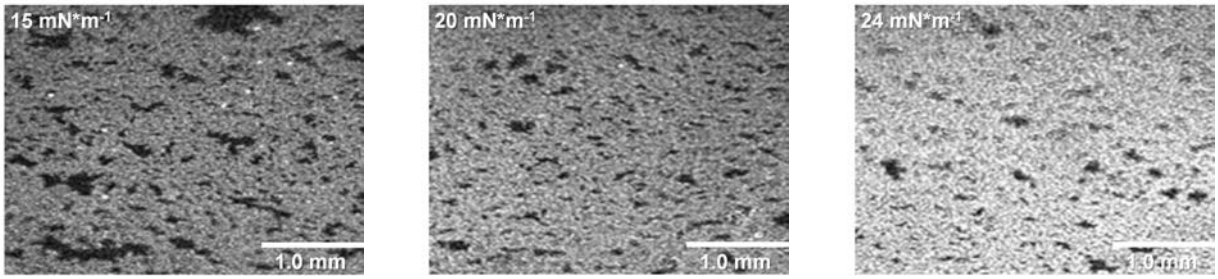


Figure 29: BAM images of OPE2A at the air-water interface at the indicated surface pressures.

In Figure 29 a rapid increase in brightness of the monolayer after the isotherm take-off is indicative of an increase of the tilt angle of the molecules with respect to the water surface.[27] In addition, an increase in the surface pressure indicates a higher surface coverage of the film.

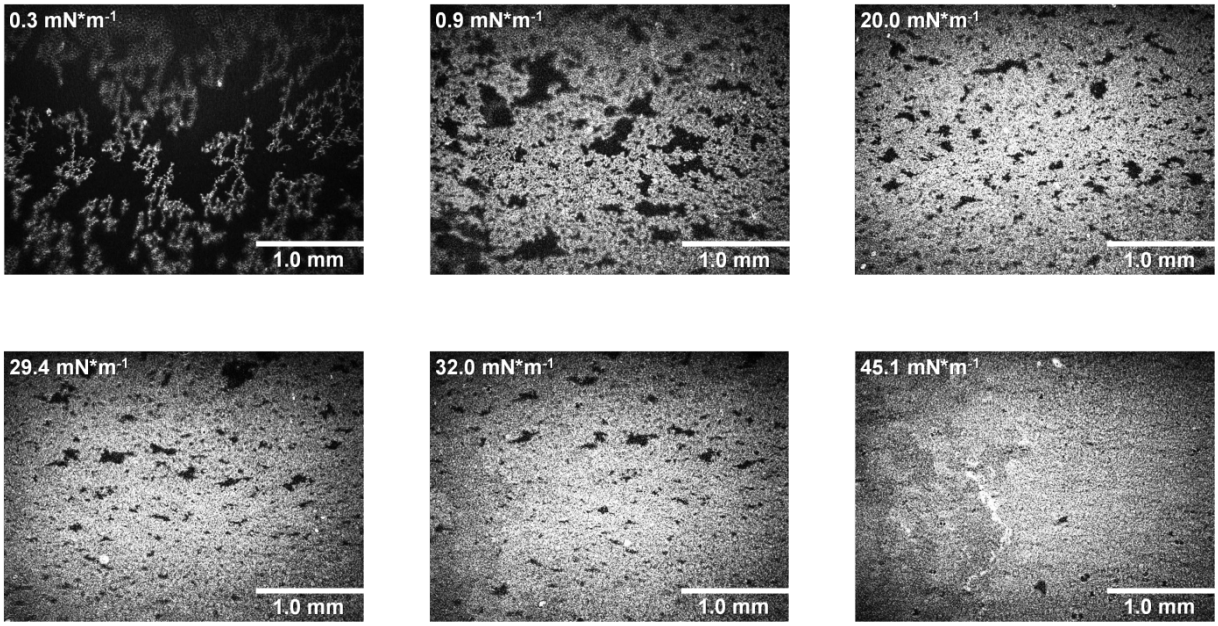


Figure 30: BAM images of OPE2A on an $AgNO_3$ aqueous subphase at the air-water interface at the indicated surface pressures.

BAM images of the monolayer onto an $AgNO_3$ aqueous subphase neither shows evidences of aggregation, and also an increase in the surface coverage and in the brightness of the film are observed upon the compression process. At high surface pressures, e.g. 45 $mN \cdot m^{-1}$, the bright lines in the image are indicative of the formation of 3-D aggregates which is in good agreements with the observations in the π-*A* isotherm.

The Langmuir films prepared onto an $AgNO_3$ aqueous subphase were transferred onto quartz substrates during the immersion process of the substrate with a transfer ratio of 0.7.

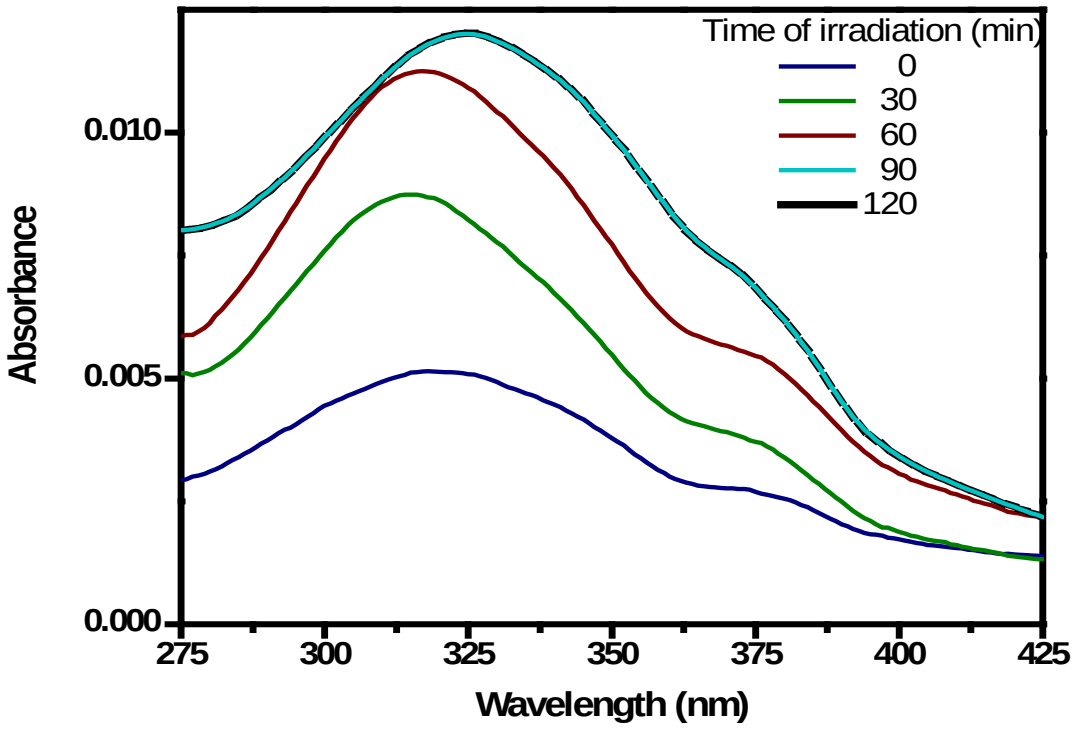


Figure 31: UV-Vis spectrum of OPE2A monolayer with silver nanoparticles on quartz substrate irradiated during different time intervals with a UV lamp (256 nm).

Although a peak cannot be observed were the silver plasmon is expected, there is an increase in the absorbance of the molecules as they are irradiated with time. A possible reason for the absence of the plasmon peak characteristic of silver could be due to the tilting of the organic molecules, which might yield a different absorbance as the angle of their physical position changes.

To obtain SEM images a monomolecular layer of OPE2A with silver nanoparticles was transferred onto a glass substrate in an up-down manner (see Figure 15). The transfer ratio for the films was between low having a maximum transfer ratio of 0.5. SEM images further

confirmed this (see Figure 32) as little to no silver nanoparticles as well as monomolecular film can be observed.

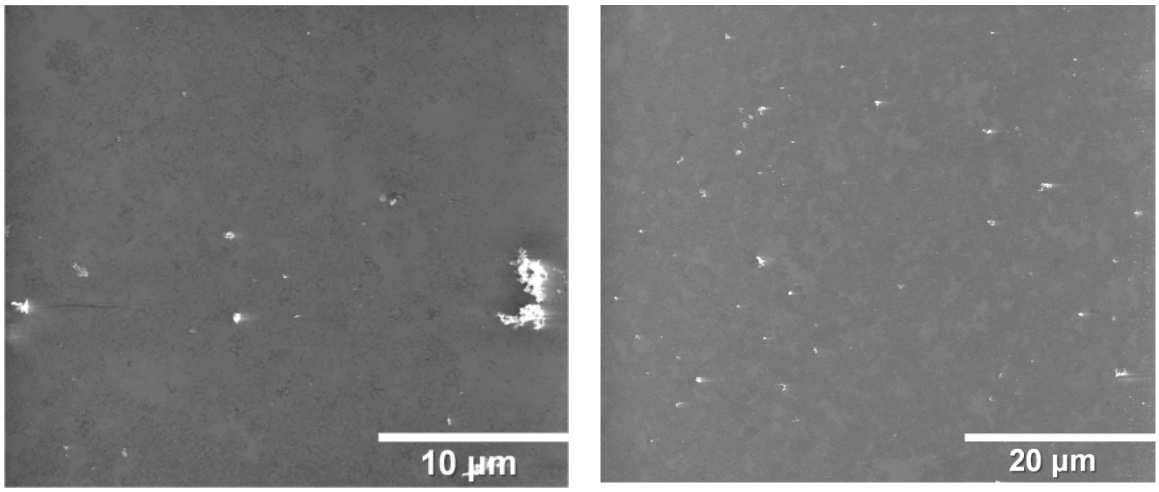


Figure 32: SEM images of OPE2A transferred onto from a 10^{-3}M subphase of $AgNO_3$ and irradiated for 90 minutes

Since the previous results were not good, the experimental procedure was then modified (see Figure 11) with the objective of fabrication a top-contact electrode. A monomolecular layer of OPE2A onto a water subphase was transferred onto a glass substrate during the emersion or immersion process with the best transfer ratio of being 0.7 and was then covered with an aqueous solution of $AgNO_3$. The substrate was then irradiated for 90 minutes and was thoroughly rinsed with Milli-Q water in order to remove any residual salt.

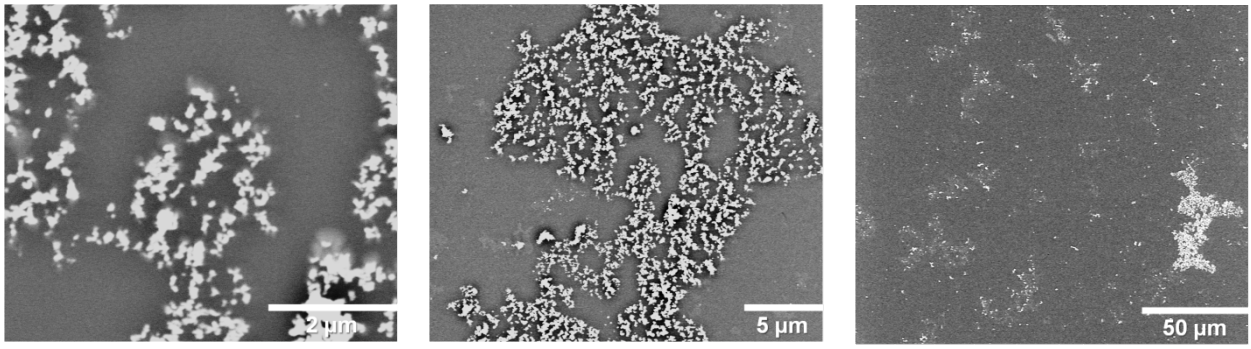


Figure 33: SEM images of OPE2A transferred onto a glass substrate via LB then treated with $AgNO_3$ for 90 minutes and washed with Milli-Q water.

SEM images of these films are shown in Figure 33 evidence the formation of metal silver clusters. These clusters and NPs are not homogeneously distributed over the whole film surface. Although a good metallic layer has not been obtained these films could work as seeds for further deposition of a metal layer using other procedures and limiting the number of short-circuits unfortunately present in the conventional so far used methods for the fabrication of the top contact electrode.

To further explore the characteristics of the metallic clusters and nanoparticles obtained by this method AFM measurements were carried out. Thus, Figures 35 and 36 shows images of an OPE2A pristine film and after the treatment previously indicated for the deposition of metal silver, respectively. A comparison of both images reveals the growth of NPs or clusters after the irradiation process with a significant increase in the film roughness.

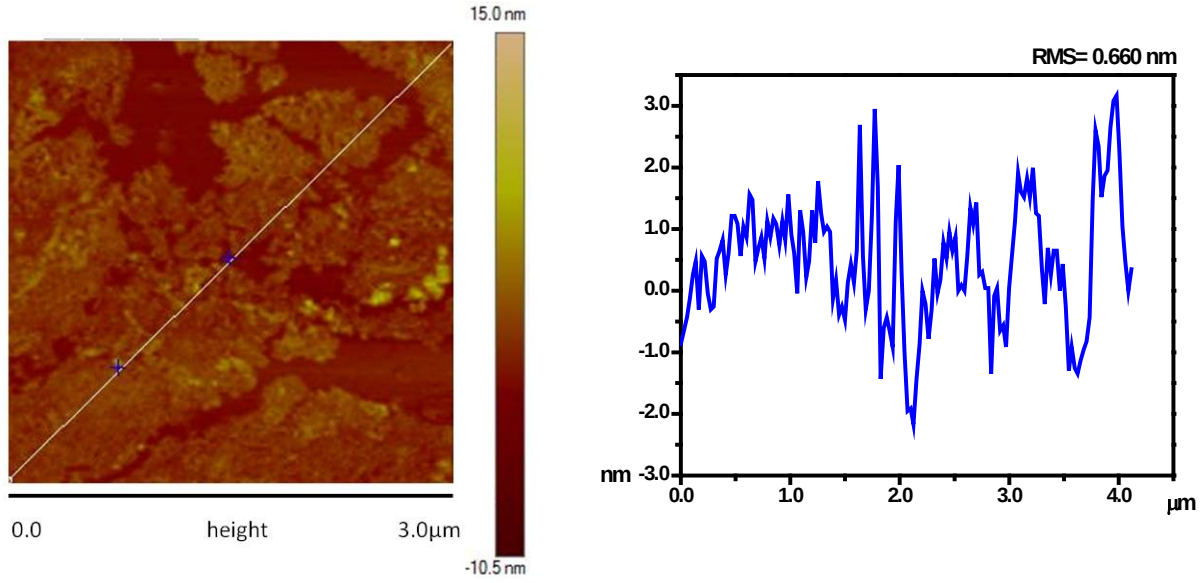


Figure 34: AFM image and section analysis of an OPE2A monomolecular pristine film transferred on mica from a pure water subphase at a surface pressure of 20 $mN \cdot m^{-1}$.

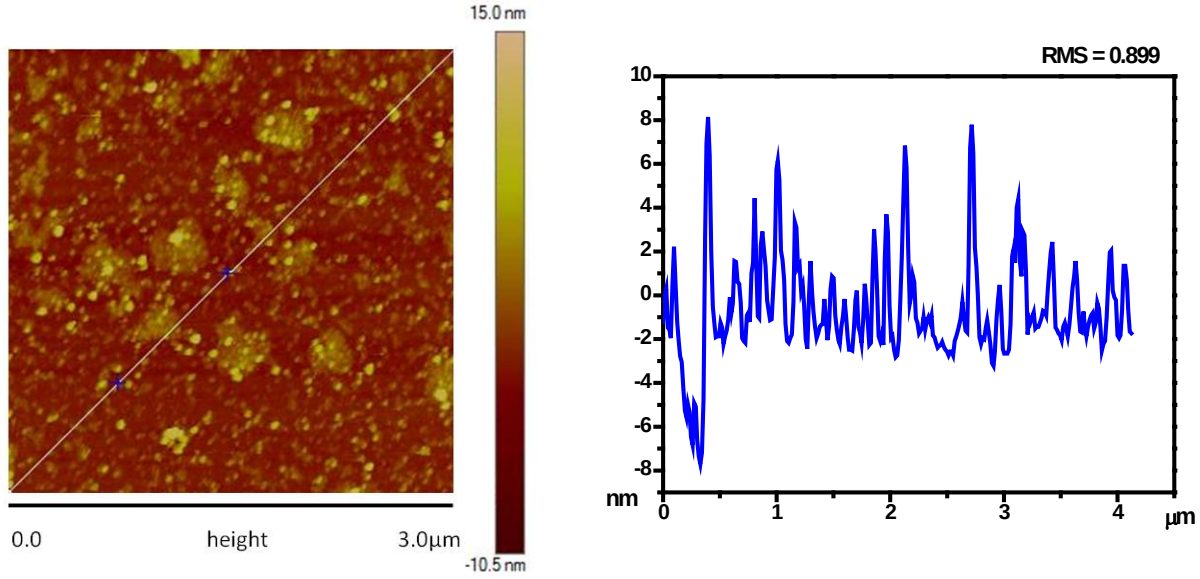


Figure 35: AFM image and section analysis of an OPE2A monomolecular film transferred on mica from a pure water subphase at a surface pressure of 20 $mN \cdot m^{-1}$, after coverage by an $AgNO_3$ aqueous subphase and irradiation for 90 minutes.

XPS measurements were taken to determine whether Ag (0) was present in the monomolecular film. The two previously discussed methods, i.e. with $AgNO_3$ present in the subphase and with only Milli-Q water, of creating an OPE2A monomolecular film with silver nanoparticles were performed on a gold substrate and characterized. This was done since the carboxylic acids adsorb on copper group metals including silver and gold.[30] This occurs as the ionizable hydrogen atom of the acid is noted to leave from the carboxylic group with the resulting carboxylate ion adsorbing with the two oxygen atoms attached to the metal surface. This process is analogous to the well investigated method of the adsorption of thiols, where the hydrogen atom is removed from the S-H group of the thiols as the S-Au bond is formed.

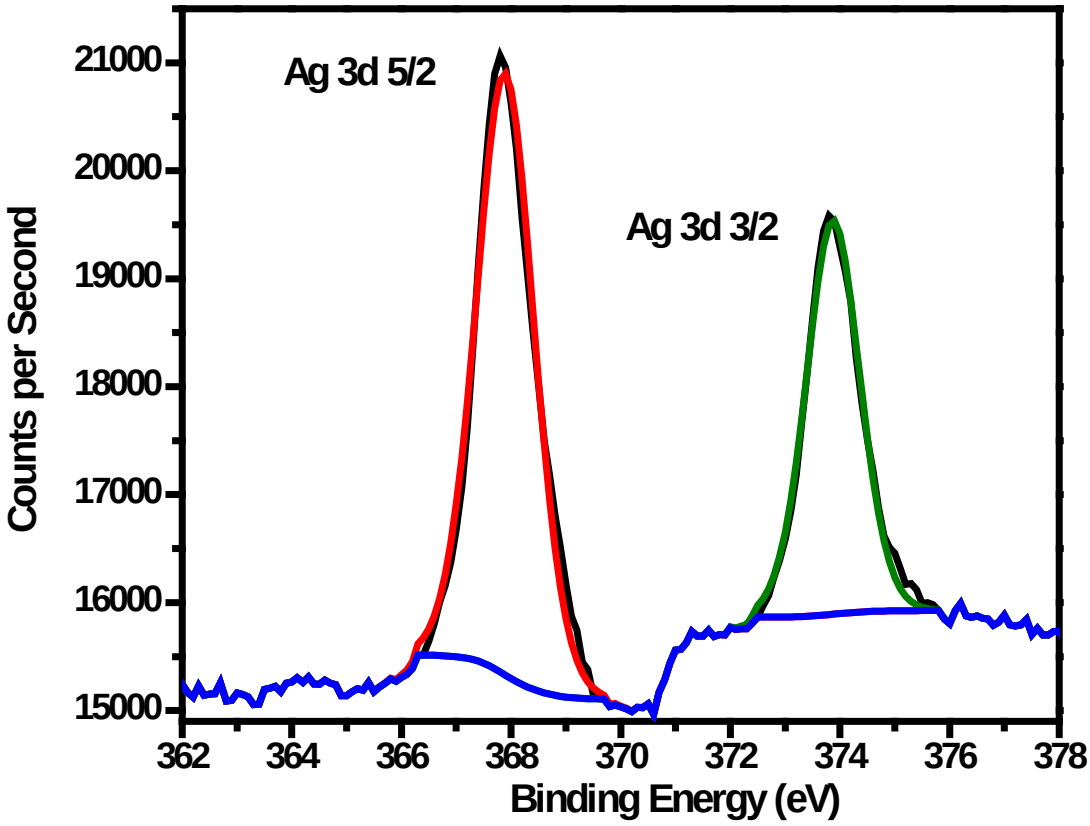


Figure 36:XPS spectrum of Ag 3d of OPE2A transferred from an aqueous $AgNO_3$ and irradiated for 90 minutes.

In Figure 35 two peaks at 367.7 and 367.7 eV can be observed and correspond to the Ag(0)3d 3/2 and Ag(0)3d 5/2 . In addition, the peak separation between both bands 6.1 eV in good agreement with the 6.2 eV literature value for the peak separation of Ag (0).[29, 30]

To further confirm the presence of Ag (0) the Auger parameter was calculated using the kinetic energy of the Auger spectra and the silver binding energy (Figure 36). The Auger parameter was found to be approximately 725.5 eV and it was calculated simply by summing the kinetic energy of the auger electron (see Figure 37) with the binding energy of the silver photoelectron. This value is found to be fairly close to the value reported in literature for Ag (0) ranging from 725.8 to 726.3.[23]

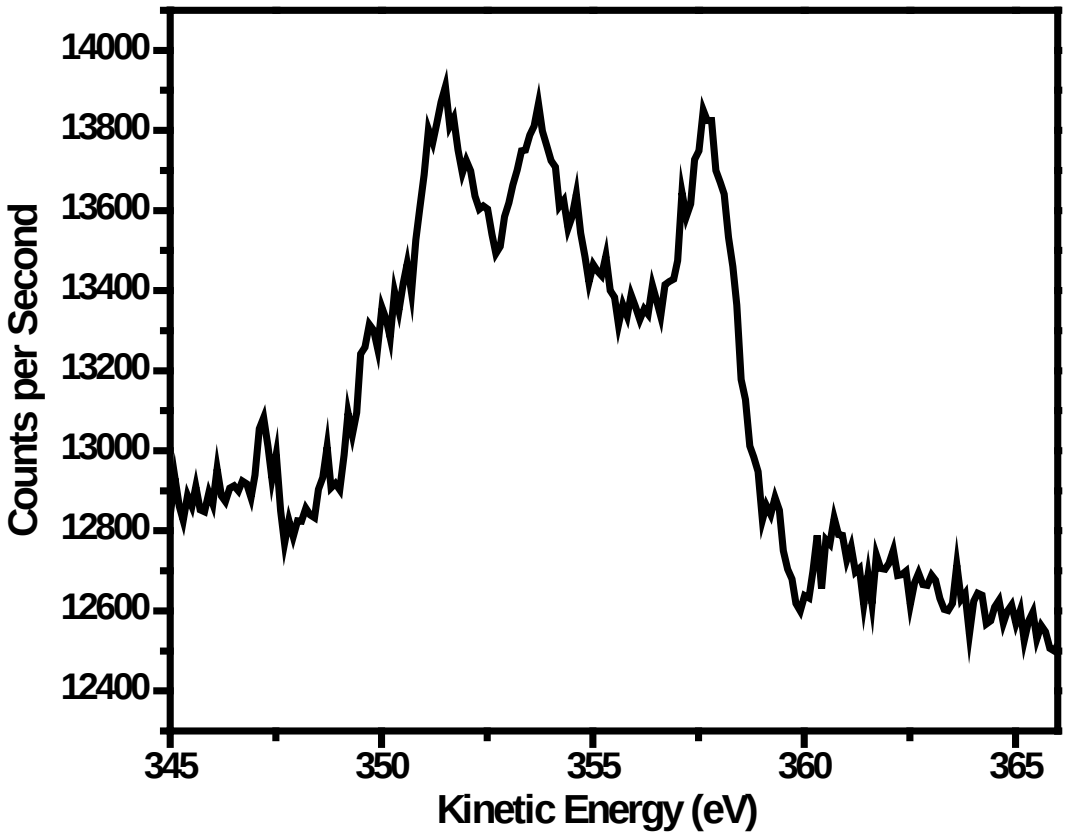


Figure 37: Auger spectrum of Ag (0) for OPE2A

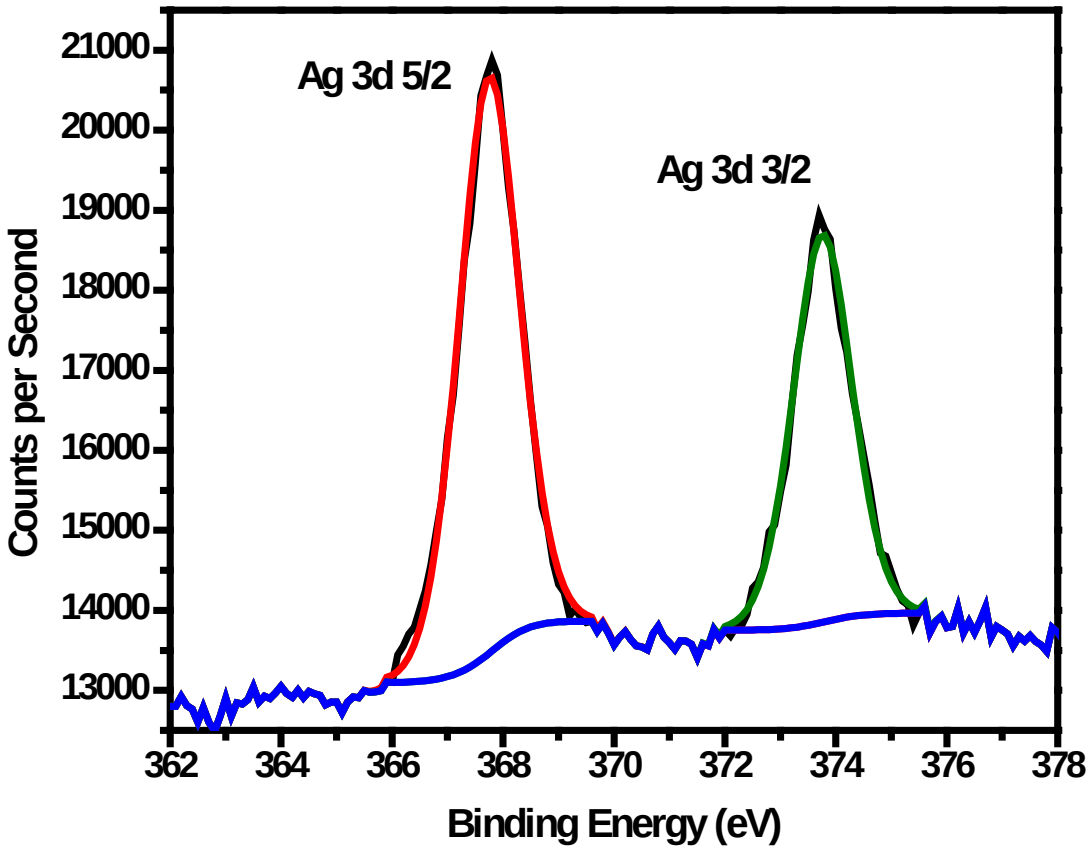


Figure 38: XPS spectra of Ag 3d of OPE2A with silver nanoparticles deposited by covering the film already deposited onto the substrate with aqueous $AgNO_3$.

Section 3.2.1: Conclusions of OPE2A

Two different ways of preparing OPE2A thin films with a silver top contact have been investigated. The first method involved using the Langmuir Blodgett method with aqueous silver as the subphase. The second method involves transferring the film onto a substrate and subsequently covering with aqueous silver. Both methods require 90 minutes of irradiation with UV light (256 nm) to photoreduce the metal precursor. In the case of this specific molecule the second method involving the subsequent treatment of aqueous silver seems to yield more positive results.

Using this method SEM results reveal the presence of silver nanoclusters present onto the transferred film. Furthermore, AFM results indicate an increase in the surface roughness of the

silver containing irradiated substrate with respect to the substrate containing only the film. This further leads to conclude that Ag (0) is placed as a top electrode. To confirm the presence of Ag (0) the films were characterized with XPS with positive results demonstrating the presence of the desired element.

Chapter 4: Conclusions

Molecular electronics is a field plagued with challenges. The most notable challenge is merging efficiently with the current silicon based microelectronics industry. Being able to further downscale the dimension of current CMOS, requires a profound knowledge of the limits of silicon based technologies, as well as the feasible solutions that molecular electronics can offer.

Most research has been geared towards using gold as a bottom substrate material due to the straightforwardness and reliability of organic monolayers built onto gold. Using gold however is not a benefit when dealing with the hybridization of technologies, this is mainly due to the nature of gold, which has propensity to form energy traps in silicon. Using gold and evaporating it to form top-contact has been shown to degrade and/or shift monolayers in junctions.

Silver is known not to show displacement of the molecular junctions when used as a top-contact. This makes silver attractive for research, and is the reason behind the choice of this metal for this project. Creating a metallic top layer deposited onto a molecular array that is reproducible, durable and compatible with silicon technologies is no easy feat. So is choosing the right molecules that can anchor well onto both substrate and top contact, while containing good electronic properties.

There are a variety of methods currently being used to fabricate a top-contact. The method used for this research was described firstly by Dr. Gorka Pera from the University of Zaragoza in his doctoral research. This method uses the Langmuir Blodgett technique to transfer a monomolecular layer containing a metal precursor onto a substrate. The substrate is then irradiated to photoreduce the metal precursor with the subsequent generation of metal clusters and NPs on the film surface. This novel method represents a cheap and efficient way of creating

a top-contact. This method is the base of this work through which a molecular junction made of behenic acid (BA) and 1,4-bis-(4-phenylethynyl)-benzene-4'-4'-bis(carboxylic acid) (OPE2A) was investigated.

In the case of BA a film containing Ag (I) as counter ions to maintain the electroneutrality of the system was efficiently transferred onto substrates and characterized by several techniques including UV-vis spectroscopy, AFM, and SEM. All these methods revealed that after irradiation of the films silver nanoparticles or silver clusters were obtained on top of the monomolecular film.

The electronic nature of OPE derivatives makes them attractive for molecular electronics, since these aromatic based molecules contain Fermi energy levels close to the energy levels of electric contacts currently used. OPE2A is an OPE derivative and a symmetric molecule which contains two carboxylic groups, one which anchors to the substrate and another which interacts with the silver ions.

Using two methods nanoparticles and nanoclusters were successfully formed onto the monomolecular film of OPE2A. The method with the best results required a subsequent treatment of aqueous silver deposited onto an OPE2A monomolecular film. This method should be further tested with other molecules containing different functional groups to investigate its practicality.

Although OPE2A does not have the same degree of homogeneity of BA, it still demonstrates the capabilities of adopting silver as a top-contact. The interaction of the carboxylic group and silver could be exploited in other compounds containing other terminal groups to anchor more efficiently to a variety of substrates.

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